Coating Processes for Columbium Alloys
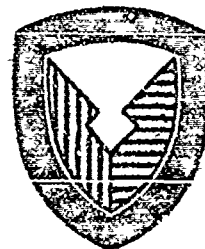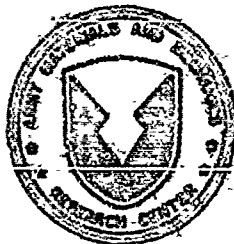
TRW Inc Cleveland Ohio

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AVSCOM REPORT NO. 76-39

Production Engineering Measures Program
Manufacturing Methods and Technology

COATING PROCESSES FOR COLUMBIUM ALLOYS

M. T. GROVES
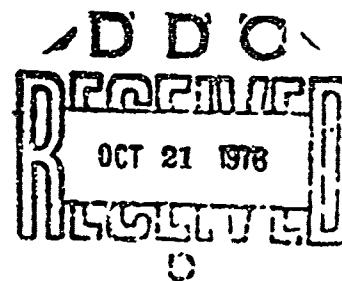TRW Inc.
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this program was to develop improved processing techniques for depositing the NS-4 coating on columbium alloys. The NS-4 coating consists of depositing a vacuum sintered modifier layer (nominal composition 20Mo-50W-15Ti-15V) and then siliciding the modifier layer. Currently, the modifier layer is deposited by manual dipping in a slurry and siliciding is accomplished by pack cementation. The objectives of this program were to develop an electrophoretic process for depositing the modifier layer and a chemical vapor deposition

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20. (continued) process for siliciding the modifier layer. Electrophoretic deposition from both waterbase and isoproponol suspensions was investigated for deposition of the modifier layer. Satisfactory deposits could not be obtained from waterbase suspensions. Gases resulting from electrolysis of the water produced defects in these deposits. Satisfactory deposits were obtained from isoproponol-nitromethane suspensions. Parameters were developed for depositing nominal modifier layer thicknesses of 2.0, 3.5 and 5.0 mils from suspensions containing total Ti+V contents of 10 w/o, 20 w/o and 30 w/o. Deposition parameters were developed for depositing silicon on the modifier layer by hydrogen reduction of $SiCl_4$. Deposition times of up to 10 hours at a temperature of 2300°F were required to produce minimal silicon contents in the modifier layer. Longer deposition times were not considered to be obtainable with the chemical vapor deposition equipment due to the extremely corrosive environment produced by the deposition conditions. Coating coupons failed within 20 hours of oxidation exposure at 2500°F. Premature failure was attributed to the low silicon content of the coupons.

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FOREWORD

This technical report covers work performed under contract number DAAG46-74-C-0097 from May 7, 1974 through November 7, 1975. This work was performed by TRW Inc., Cleveland, Ohio 44117 under the technical supervision of Dr. Milton Levy of the Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172.

This project was accomplished as part of the U.S. Army Aviation Systems Command Manufacturing Technology program. The primary objective of this program is to develop, on a timely basis, manufacturing processes, techniques, and equipment for use in production of Army materiel.

Comments are solicited on the potential utilization of the information contained herein as applied to present and/or future production programs. Such comments should be sent to: U.S. Army Aviation Systems Command, ATTN: AMSAV-EXT, P.O. Box 209, St. Louis, Missouri 63166.

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1.0 SUMMARY

This work was undertaken to develop improved processing techniques for depositing the NS-4 coating on columbium alloys. The NS-4 coating consists of a sintered modifier layer (nominal composition 20Mo-50W-15Ti-15V) that is subsequently silicided. The current deposition process consists of depositing the modifier layer by manual dipping in a slurry, sintering and then siliciding by pack cementation. The objective of this program was to improve the thickness uniformity, decrease the labor and increase the low material usage associated with these deposition processes. Electrophoretic deposition was investigated as an alternate technique for depositing the modifier layer and chemical vapor deposition was investigated as an alternate technique for siliciding the modifier layer. Using these techniques, the NS-4 coating was deposited on 20 and 40 mil thicknesses of columbium alloy FS-85. After these techniques were developed, they were to be used to evaluate the effect of modifier layer chemistry and thickness, sintering temperature and silicon content on the oxidation resistance and mechanical properties of the NS-4 coating.

Electrophoretic deposition from both waterbase suspensions and isoproponol-nitromethane suspensions was investigated for deposition of the modifier layer. Initially, deposits were made from the waterbase suspensions using a constant applied potential. Gases resuiting from electrolysis of the water produced large numbers of defects in these deposits. Additional deposition trials were made with the waterbase suspensions in which the applied potential was pulsed such that the polarity was reversed on alternate pulses. The object of cyclically reversing the applied potential was to repel gaseous ions in the vicinity of the work piece as well as allow the discharged ions to escape. Using the pulsed-reversed potential technique, the defects could be minimized but not completely eliminated in deposits made from waterbase suspensions. Efforts were then directed towards developing parameters for electrophoretically depositing the modifier layer from isoproponol-nitromethane suspensions.

Satisfactory electrophoretic deposits were obtained from isoproponol-nitromethane suspensions. Parameters were developed for depositing nominal modifier layer thicknesses of 2.0, 3.5 and 5.0 mils from suspensions containing total Ti+V contents of 10 w/o, 20 w/o and 30 w/o. These modifier layer deposits were sintered for 15 hours at temperatures of $2760^{\circ}F$ or $2940^{\circ}F$. There was no detectable

difference in modifier layer thickness through vaporization losses or more complete sintering at the higher temperatures.

Parameters were developed for depositing silicon on the modifier by hydrogen reduction of $SiCl_4$. The effect of a number of processing variables on the silicon to modifier atomic ratio was investigated during the parameter development work. These variables included modifier thickness and composition, $H_2/SiCl_4$ ratio, reaction chamber pressure and deposition time. Decreases in modifier thickness, modifier Ti+V content and the $H_2/SiCl_4$ ratio increased the silicon to modifier atomic ratio. Increases in reaction chamber pressure up to 0.400 atm increased the silicon to modifier atomic ratio. The effect of deposition time was dependent on reaction chamber pressure. Increasing the deposition time at a pressure of 0.167 atm increased the silicon to modifier atomic ratio to a limiting value. Increasing the deposition time at a pressure of 0.400 atm increased the silicon to modifier atomic ratio for all deposition times utilized in the experiments.

The objective of the chemical vapor deposition parameter development was to determine parameters for producing silicon to modifier atomic ratios of >2.1, 2.5 and 3.0 in modifier thickness levels of 2.0, 3.5 and 5.0 mils. Deposition times of up to 10 hours at a deposition temperature of 2300°F were required to produce silicon to modifier atomic ratios of >2.0 in 2.0 mil thick modifier layers. Deposition times of 15-20 hours were projected for obtaining the required silicon to modifier atomic ratios for the thicker modifier layers. These deposition times were not considered to be obtainable with the present chemical vapor deposition equipment. Extensive modification of the equipment to better withstand the severe service environment would be required to obtain the extended deposition times. Modification of the equipment was not possible within the program funding and schedule. A number of coated coupons with 2.0 mil modifier layers and silicon to modifier atomic ratios of >2.1 were oxidation tested at 2500°F. All of the coupons failed within 20 hours of exposure. Premature failure was attributed to the low silicon content of the coatings.

2.0   INTRODUCTION

As inlet gas temperatures increase in higher performance gas turbines, conventional nickel and cobalt base superalloys will no longer meet the strength requirements of blade and vane materials. Air cooling is used to reduce metal temperature, however, bleeding the compressor discharge for cooling reduces engine efficiency. More sophisticated air cooling schemes envisioned for future engine design utilizing superalloys will be expensive and difficult to fabricate. The use of coated columbium alloys in blades and vanes would reduce cooling requirements for high thrust-low weight gas turbines for military applications.

Alloy development efforts have resulted in a number of commercially available columbium alloys that possess good high temperature mechanical properties. Significant progress has also been made in the development of high temperature protective coatings for columbium alloys and other refractory metal alloys. One of the advanced coatings is the NS-4 coating developed by Solar under NASA sponsorship[1][2]   The NS-4 coating on columbium alloy FS-85 has exhibited a cyclic furnace oxidation life of more than 800 hours at 2400°F and an oxidation-erosion rig test life (Mach .85) of over 200 hours at 2400°F. This coating consists of a modifier layer (nominal composition 20Mo-50W-15Ti-15V) applied by a vacuum sintered slurry followed by siliciding with pack cementation. Currently, the modifier layer is deposited by manual dipping in a slurry. This process is costly and results in large thickness variations, particularly on internal surfaces. Siliciding is currently done by using pack cementation. In pack cementation processes, coating material utilization is low and deposition of coatings in internal surfaces requires that pack material be manually placed in each opening and removed after the siliciding cycle.

Electrophoretic deposition of the modifier layer has the potential to improve both the process economics and the thickness uniformity of the modifier layer. Electrophoretic deposition describes those processes in which insoluble particles move under the influence of an electrical field applied to the medium that suspends the particles. The origin of the electrophoretic effect is the disturbance of charged double layers attached to solid particles by the applied potential. Electrophoretic deposition is distinguished from the more familia-

electroplating proce: in that particles rather than ions are deposited on one
of the electrodes. Extensive reviews of the principles of electrophoretic
deposition can be found elsewhere[3][4].

Electrophoretic systems using either water or organic liquids as suspending
media have been the most widely used in industrial applications. Waterbase depo-
sition processes utilize a suspension of insoluble phases in water containing a
soluble resin complex. Typically, the resin complex consists of a malcinized oil
or organic solvent, soluble polycarboxylic acid resin and an alkaline (KOH, amine
or ammonia) solubilizing agent. Electrode reactions occurring in the deposition
bath are shown schematically in Figure 1 for a waterbase suspension containing an
amine-solubilized resin[5]. The overall deposition process involves not only
electrophoresis but other electrokinetic phenomena which include electro-osmosis,
electrolysis and electro-deposition. Presence of the electrical field produces
electrophoretic migration of the suspended particles to the anode where the
particles are deposited by electro-deposition. The deposit is concentrated and
dewatered by electro-osmosis. Simultaneous electrolysis of water results in
evolution of oxygen and H^+ at the anode. At a metallic anode, additional reactions
that can occur include electro-dissolution of the anode, the formation of organo-
metallic complexes between ions resulting from this dissolution and the resin, and
decarboxylation and cross-linking of the resin such as the Kolbe reaction. These
phenomena arise from localized decreases in pH in the vicinity of the anode.

Processes using electrophoreses to deposit particles involve coating the
metallic particles with resin. The coated particles then assume the double charge
layer characteristic of the resin complex and the resin/particle bisque is
deposited at the anode. Subsequent heating at an elevated temperature can be
used to drive off any water not removed by electro-osmosis and the resin to
provide a coating of sintered particles. The most common use of waterbase
suspensions is to deposit pain. pigment[6]; however, waterbase suspensions have
also been used to deposit aluminide coating bisques[7][8].

Non-aqueous suspension media have been used in order to eliminate or
decrease electrolysis. In non-aqueous suspensions, particle charging is usually
accomplished by an absorbed ion complex such as the protein molecule obtained

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CATHODE (-)   ANODE (+)

$NR_2H_2{}^+$ $RCOO^-$ →

SOLUBILIZED AMINE COMPLEX

$NR_2 H + H_2O \longrightarrow NR_2 H_2{}^+ + OH^-$ $RCOO^- + H^+ \longrightarrow RCOO H$ COAGULATION

$2H^+ + 2e^- \longrightarrow H_2$ $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$ GAS FORMATION

$2H^+ + 2e^- \longrightarrow H_2$ $Me \longrightarrow Me^{n+} + ne^-$ ANODE DISSOLUTION

$nRCOO + Me^{n+} \longrightarrow Me(RCOO)n$ METAL COMPLEX
                                              FORMATION

$RCOO^- \longrightarrow R + e^- + CO_2$ DECARBOXYLATION

$R + R \longrightarrow RR$ KOLBE REACTION
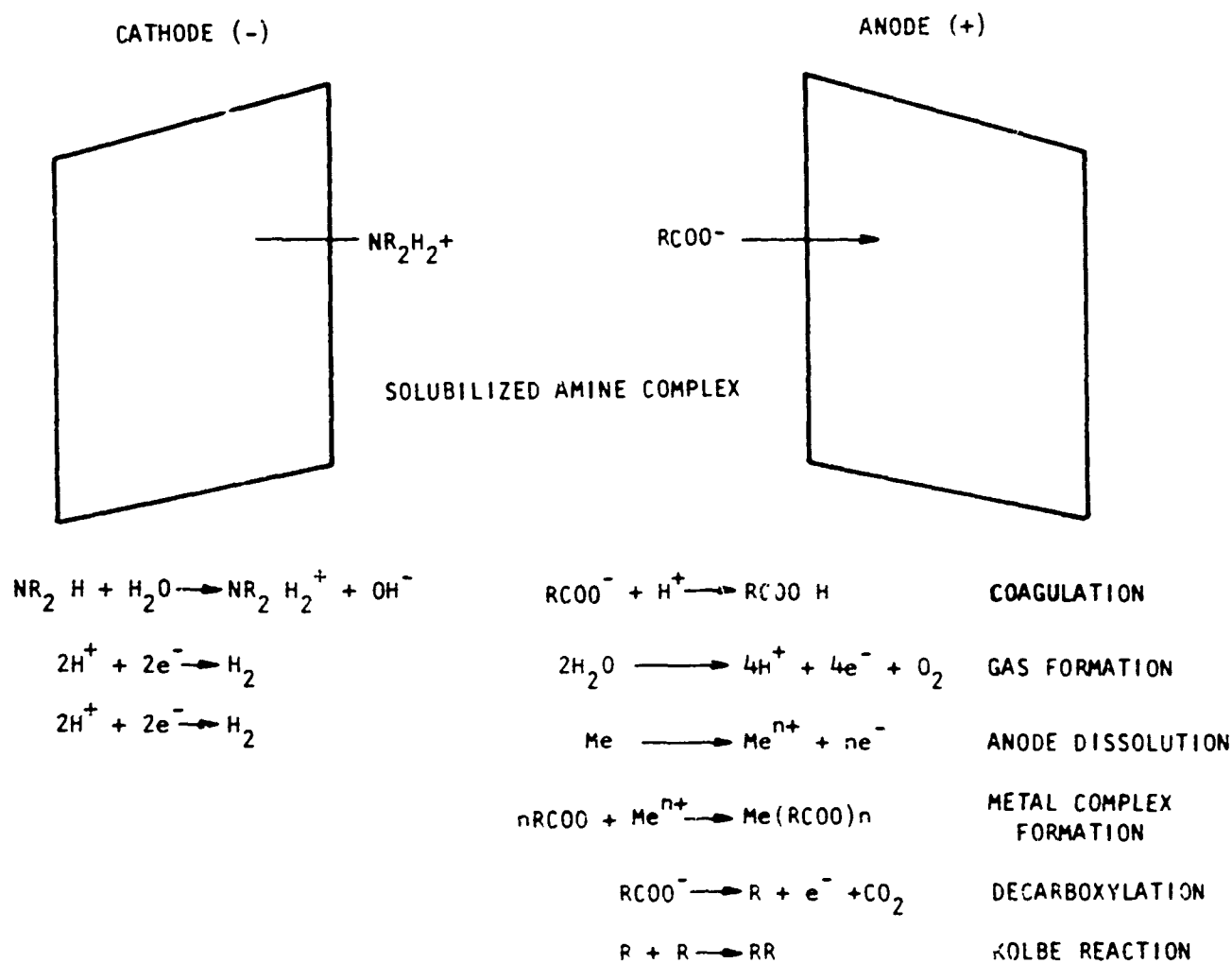
Figure 1. Electrode Reactions in a Water-Base Suspension.[5]

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from zein. A variety of particles have been electrophoretically deposited from a variety cf non-aqueous suspension mediums. Alcohol has been used as a suspenaing medium to deposit nickel, nickel-chromium and nickel-chromium-iron coating by Shyne et al[9]. Lamb and Reid[10] were able to deposit aluminum silicon, germanium, GeO_2, WO_3, NiO, $BaTiO_3$ from diethylene glycol dimethylether and pyridine and Pearlstein et al[11] deposited aluminum from suspensions in butyl amine. Isoproponol-nitromethane suspensions have been used to deposit refractory metals, carbides, oxides, a $W-TiH_2$ mixture, and aluminide coating bisques[12-14].

Chemical vapor deposition of silicon by the hydrogen reduction of $SiCl_4$ has the potential to improve the process economics of siliciding the modifie. layer. Hydrogen reduction of $SiCl_4$ to produce high purity silicon for semi-conductor processes is an established process. Success in this area has led workers to consider the process for producing oxidation resistant silicide coatings on refractory metals. Using hydrogen reduction of $SiCl_4$, Beidler et al[16] produced molybdenum disilicide coatings on molybdenum and Wakefield[17] silicided the Cr-Ti modifier layer of the Cr-Ti-Si coating on columbium alloys.

The objectives of this program were to develop an electrophoretic process for depositing the modifier layer and a chemical vapor deposition process for siliciding the modifier layer by hydrogen reduction of $SiCl_4$. The developed processes were then to be used to evaluate the effect of coating variations on oxidation resistance and mechanical properties of the coating and determine the optimum combination of oxidation resistance and mechanical properties. The Solar work indicated that the NS-4 coating could tolerate a considerable variation in coating chemistry and thickness yet still provide good oxidation protection. Coating chemistry variations included variations in the Ti+V content of the modifier layer and silicon content of the coating. Increasing the Ti+V content of the modifier layer improved mechanical properties but decreased oxidation resistance. Ti+V content was also related to the sintering temperature. Solar utilized sintering temperatures in the range of $2760^{\circ}F$ to $2940^{\circ}F$. Increasing the sintering temperature increased the loss or titanium and vanadium in the modifier layer. Primary oxidation protection was provided by the silicon. It was determined that the silicon to modifier layer atomic ratio must be at least >2.1 to provide satisfactory oxidation protection. Coating thickness variations

of 3.2 to 5.0 mils did not seriously affect mechanical properties of the substrate
In view of the considerable tolerance in coating chemistry and thickness, the
following nominal variations were chosen to determine the optimum combination of
oxidation resistance and mechanical properties on the present program:

1. Sintered Modifier Layer Thickness - 2.0, 3.5 and 5.0 mils.

2. Modifier Layer Ti+V Content -
        Modifier layer to be deposited from suspensions
        containing Ti+V contents of 10, 20 and 30 w/o.

3. Sintering Temperatures - 2760, 2830 and 2940°F.

4. Silicon Content - silicon to modifier atomic ratios of
    >2.1, 2.5 and 3.0.

3.0   EXPERIMENTAL PROGRAM

The experimental program was divided into a number of tasks. The objectives of these tasks were as follows:

Task 1.0:   Develop Electrophoretic Deposition Parameters for Depositing the Modifier Layer.

Deposition parameters were to be developed for depositing the sintered modifier layer by electrophoresis. Specifically, deposition parameters were to be established for producing nominal modifier layer thicknesses of 2.0, 3.5 and 5.0 mils after sintering at $2760^\circ F$, $2830^\circ F$ and $2940^\circ F$ in vacuum at three levels of Ti+V content (10, 20 and 30 w/o).

Task 2.0:   Develop Chemical Vapor Deposition Parameters for Siliciding the Modifier Layer.

Chemical deposition parameters were to be developed for siliciding the modifier layer using hydrogen reduction of silicon tetrachloride. Specifically, deposition parameters were to be established for producing nominal silicon to modifier layer atomic ratios of >2.1, 2.5 and 3.0.

Task 3.0:   Factorial Experiment.

Using deposition parameters developed in Tasks 1.0 and 2.0, a factorial experiment was to be performed to investigate the effect of modifier layer thickness, modifier layer composition, sintering temperature and silicon content on oxidation resistance and mechanical properties.

Task 4.0:   Coat Complex Shapes.

Coatings selected from the results of Task 3.0 were to be deposited on a simulated vane configuration.

Difficulties with the chemical vapor deposition equipment in Task 2.0 prevented completion of Tasks 3.0 and 4.0. As a result, only a minor amount of oxidation testing was performed in Task 3.0 and no work was performed in Task 4.0.

3.1 Substrate Materials and Specimen Preparation

The substrate material used in this program was the FS-85 alloy
(Cb-28Ta-10.5W-0.9Zr) supplied by Fansteel Metals in the form of 20 and 40 mil
sheet. All of the material was the product of one heat. A vendor certified
heat analysis for the material is shown in Table I. Specimens for parameter
development and oxidation tests consisted of 0.750 inch x 0.750 inch coupons
sheared from the sheet. Initially, coupons were prepared for coating by tumbling
and then etching in a 45 v/o HNO_3 - 45 v/o H_2SO_4 - 10 v/o HF solution. Later it
was found that a more desirable edge for coating could be obtained if the sheared
edges were surface ground prior to tumbling. Bend test specimens (t x 1.0 inch x
4.0 inch) were also prepared using the same preparation techniques as for the
coupons.

3.2 Development of Electrophoretic Deposition Parameters

The objective of this phase of the work was to develop electrophoretic
deposition parameters for depositing the W-Mo-Ti-V modifier layer. The modifier
layer was deposited using three variations of Ti and V content in the coating
powder; 64.3 w/o W + 25.7 w/o Mo + 5 w/o Ti + 5 w/o V (Ti+V = 10), 57.1 w/o
W + 22.9 w/o Mo + 10 w/o Ti + 10 w/o V (Ti+V = 20) and 50 w/o W + 20 w/o Mo +
15 w/o Ti + 15 w/o V (Ti+V = 30). In each instance, the ratio of W to Mo was 5/2.
Parameters were developed to produce nominal modifier layer thickness of 2.0, 3.5
and 5.0 mils for each of the powder compositions after sintering at 2760°F, 2830°F
and 2940°F. Initial work was done with waterbase suspensions. Waterbase suspensions
are preferred to organic suspensions in industrial operations due to potential fire
and waste disposal problems associated with high concentrations of volatile organic
solvents. Uniform deposits, however, could not be obtained from the waterbase
suspensions, and the deposition parameters were developed using isoproponol-nitro-
methane suspensions. The results obtained from both suspension systems are
described below.

3.2.1 Modifier Layer Coating Powder Preparation

Elemental powders were used in all of the electrophoretic suspensions.
Average particle sizes, as determined by a Fisher Sub-Sieve Sizer, and chemical
compositions of the powders are listed in Table II. Particle sizes of the tungsten

TABLE I

VENDOR CERTIF'ED HEAT ANALYSIS OF SUBSTRATE MATERIAL

Element	Content (ppm unless otherwise noted)
Ta	28.0 w/o
W	10.7 w/o
Zr	0.82 w/o
Mo	210
Ti	<50
Fe	<50
Ni	<50
Si	<50
Cr	<50
V	<50
B	<10
Hf	<100
C	24
O	94
N	31
H	<5
Cb	Balance

TABLE II

COATING MATERIALS

Material	Vendor	Condition(a)	Particle Size(b) (microns)	Chemical Element (ppm)															
				Si	Fe	Cr	Ni	Cu	Mn	Mg	Sn	Al	Ca	Mo		C	N	O	H
W(c)	GE	A	5.30	15	37	4	6	3	<6	<3	<6	<6	<3	59	-	-	-	314	-
Mo(c)	GE	A	3.10	15	33	8	<5	<5	<10	12	81	<3	27	-	95	24	-	3204	-
Ti	RMI	A	19.40	-	500	-	-	-	-	-	-	-	-	-	-	170	48	245	792
Ti	RMI	H	-	-	-	-	-	-	-	-	-	-	-	-	-	-	11?	740	>2000
Ti	RMI	B	1.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
V	AEE	A	0.30	-	200	-	-	-	-	-	-	-	-	-	-	92	19	4500	82
V	AEE	H	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
V	AEE	B	2.15	-	-	-	-	-	-	-	-	-	-	-	-	-	940	2400	>2000

NOTES: (a) A - As Received

  H - Hydrided

  B - Ball Milled

(b) Fisher Sub-Sieve Sizer

(c) Vendor Supplied Chemical Analysis

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and molybdenum powders were 5.30 and 3.10 microns, respectively, in the as-received condition. No further preparation was done on these powders. Titanium and vanadium powders were prepared for the electrophoretic suspensions by hydriding and then ball milling to reduce their particle sizes. Hydriding was carried out in Inconel retorts that were vacuum-argon purged three times at room temperature, back filled with 3 psig hydrogen and then placed in pre-heated furnaces. The retort containing titanium was placed in a furnace pre-heated to 800°F. The furnace was then brought up to 1200°F and the retort was soaked at 1200°F for 10 hours. The retort containing vanadium was placed in a furnace pre-heated to 1200°F. The furnace was then brought up to 1700°F and the retort was soaked at 1700°F for 8 hours. Hydrogen flow was adjusted during the hydriding cycles to maintain a pressure of approximately 3 psig. Hydrogen pressure was maintained while the retorts were removed from the furnace and allowed to cool to room temperature. Hydriding increased the hydrogen content of both the titanium and vanadium to greater than 2000 ppm. Nitrogen content was also increased in both elements, while oxygen content was increased in the titanium but decreased in the vanadium.

Both the titanium and vanadium powders were ball milled in de-ionized water. Ball milling for 24 hours reduced the average particle size of the titanium from 19.4 microns to 1.20 microns while the average particle size of the vanadium was reduced from 9.30 to 2.15 microns.

3.2.2   Waterbase Electrophoretic Suspensions

3.2.2.1   Procedure

Electrophoretic deposits were made from suspensions containing elemental metal powders (W, Mo, Ti and V), and electro-coating resin (Glidden No. 65137), a wetting agent (Orvus AB, Proctor and Gamble), glycerin and de-ionized water. Suspension volume was approximately 500 ml. Total metal powder content was varied from 5 w/o to 15 w/o of the total suspension weight and was one of three compositions: 64.3 w/o W + 25.7 w/o Mo + 5 w/o Ti + 5 w/o V (Ti+V = 10), 57.1 w/o W + 22.9 w/o Mo + 10 w/o Ti + 10 w/o V (Ti+V = 20) or 50 w/o W + 20 w/o Mo + 15 w/o Ti + 15 w/o V (Ti+V = 30). Resin content was proportional to the total metal content. The metal-to-resin ratio varied from 2.0/1 to 40.0/1. Wetting agent content was maintained at 0.001 w/o of the total suspension weight. Glycerin content was varied from 2.0 to 3.5 w/o.

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The suspensions were held in beakers and agitated with a magnetic stirrer during the deposition trials. A conforming cathode consisting of a screen with a rectangular cross section of 1.75 inches x 2.5 inches x 4 inches surrounded by the specimen is shown in Figure 2. Applied potentials were provided by a DC power supply. For the majority of the deposition trials, the polarity was maintained as shown in Figure 1; i.e., the specimen was positive and the cathode was negative. In the deposition trials the applied potential was varied over the range of 25 to 150 volts, while deposition time was maintained at 30 seconds. Gases resulting from electrolysis of the water produced defects in deposits made with a constant potential. In an attempt to eliminate the defects, some deposition trials were made with a pulsed reversed potential. The potential was pulsed and reversed such that a complete cycle consisted of a deposition pulse (specimen polarity positive) and a repulsion pulse (specimen polarity negative) to repel gaseous ions in the vicinity of the work piece. For these trials, the deposition potential was varied from 30 to 100 volts while the repulsion potential was varied from 1.0 to 3.0 volts. The times for both the deposition pulse and the repulsion pulse were varied from 0.17 seconds to 0.50 seconds while the total deposition time was maintained at 60 seconds. All of the electrophoretic deposits from waterbase suspensions were rinsed in water after removal from the bath to remove any non-adherent particles.

3.2.2.2 Results

The results of deposition trials from waterbase suspensions with a constant applied potential are presented in Table III. Metal powder and resin content variations provided a wide range of suspension pH and resistivity for the deposition trials. Suspension pH varied from 4.1 to 8.5 and suspension resistivity varied from 140 to 410 ohm-cm. The applied potential was varied from 25 to 150 volts. Deposition time was maintained at 30 seconds. This time was sufficient to reach a low constant level characteristic of electrophoretic deposition processes.

High metal-to-resin ratios of 40/1, 20/1 or 10/1, e.g., suspension numbers 1, 2 and 3, produced no deposits, non-adherent deposits (washed off) or incomplete coverage (large areas with no coating). The remainder of the suspensions containing metal-to-resin ratios of 2.5/1 or 5.0/1 provided adherent deposits. Deposits from all suspensions, however, contained small defects that appeared to
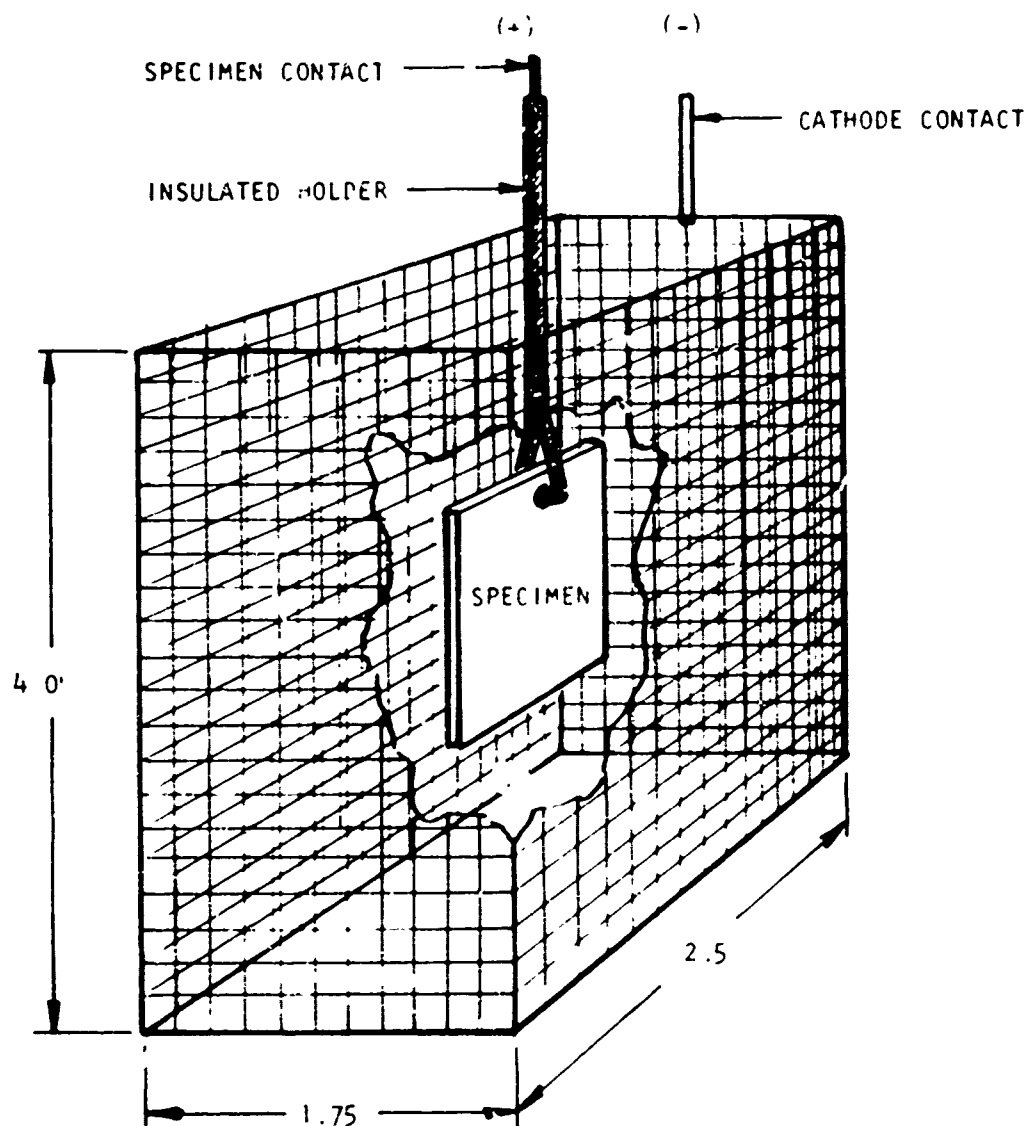
Figure 2. Conforming Cathode Used for Electrophoretic
Deposition of Modifier Layer.

TABLE III

RESULTS OF ELECTROPHORETIC DEPOSITION TRIALS WITH WATERBASE SUSPENSIONS

Suspension No.	Suspension Composition(a)				pH	Resistivity (ohm-cm)	Deposition Characteristics			Comments
	Metal w/o	Ti+V w/o(b)	Resin w/o	Metal/Resin Ratio			Volts	Time (sec)	Wt. Gain (mg/cm²)(c)	
1	15	10	0.375	40/1	4.1	410	50 / 75 / 100	30 →	- / - / -	No Deposit / " / "
2	15	10	0.75	20/1	4.8	300	50 / 100 / 150	30 →	- / 6.7 / 23.3	No Deposit / Non-Uniform Coverage / "
3	15	10	1.5	10/1	6.0	170	50 / 100 / 150	30 →	- / - / -	Deposit Washed Off / " / "
4	15	10	3.0	5/1	7.6	155	50 / 75 / 100	30 →	28.4 / 41.7 / 86.7	Uniform Coverage – few pits / " more pits / " many pits
5	15	10	6.0	2.5/1	8.3	155	50 / 40 / 30 / 25	30 →	-	Pitting/Nodules / Decreased Pitting – Nodules / " / Pitting Minimized
6	10	10	2.0	5/1	7.8	220	70 / 60 / 50 / 40	30 →	- / - / 22.8 / 22.8	Pits, Streaks, Nodules / Streaks / Pits, Streaks / Reduced Voids & Streaks
7	10	10	4.0	2.5/1	7.8	140	100 / 75 / 50 / 40 / 30	30 →	- / - / 7.4 / - / -	Numerous Areas of Pitting / " / " / Decreased Pitting / Decreased Pitting & Streaks / Light Deposit – a few pits & streaks

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TABLE III (continued)

Suspension No.	Suspension Composition (a)				pH	Resistivity (ohm-cm)	Deposition Characteristics			Comments
	Metal w/o	Ti+V w/o(b)	Resin w/o	Metal/Resin Ratio			Volts	Time (sec)	Wt. Gain (mg/cm2) (c)	
8	5	10	1.5	5/1	8.3	380	100 75 50 30	30 →	- - - -	Numerous Areas of Pitting Decreased Pitting; Streaks Light Deposit - few pits " "
9	5	10	2.0	2.5/1	8.3	275	120 90 70 50 30	30 →	- - - -	Numerous Pits " Large Streaks Pitting & Streaks Decreased Pitting & Streaks
10	15	20	3.0	5/1	8.5	185	70 50 30	30 →	- - -	Pitting Decreased Pitting Few Pits
11	15	20	6.0	2.5/1	8.5	150	50 30	30 →	- -	Few Pits " "

NOTES: (a) Balance of suspension was de-ionized water to which 0.001 w/o Orvus and 2.5 w/o glycerin was added.

(b) For Ti + V = 10 metal composition was 25.7 Mo-64.3W-5Ti-5V.

(c) Weight gain after washing and drying (3 hr/200°F).

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the naked eye in the shape of circles (pits) or lines (streaks). In many cases, the substrate was exposed at the site of the defect. Examples of these defects are shown in Figure 3. Figure 3(a) shows an example of pitting defects, while both the pitting and streak types of defects are shown in Figure 3(b). Closer examination of the streaks shows that a streak consisted of a number of pits in a line configuration. In any given suspension, the number of pits and/or streaks increased with increases in applied potential. Even at the lowest applied potentials (25 and 30 volts), however, pits and streaks were still produced in the deposits.

Pitting and streaking in electrophoretic deposits from waterbase suspensions have been attributed to electrolysis of the water[18-20]. Hydrogen or oxygen ions migrate to the work piece, are discharged and then accumulate at the work piece. When sufficient pressure is obtained in a local area, the deposited film ruptures. The particular ion that migrates to the work piece depends upon its polarity. Specimens in the present work had a positive polarity and therefore oxygen would be responsible for the pits and streaks. A number of different techniques have been reported to eliminate or decrease pitting and streaking in electrophoretic deposits from waterbase suspensions. These include the following: (a) cyclic removal and re-insertion of the work piece from the suspension during deposition to allow the gas to escape[18], (b) pulsing the potential to allow the gas to escape when the potential is zero[19] and (c) pulsing and reversing the potential to repel gaseous ions in the vicinity of the work piece as well as allow the discharged ions to escape[20]. The last technique, pulsing and reversing the potential, was chosen for additional deposition trials with the waterbase suspensions.

The results of deposition trials from waterbase suspensions with a pulsed-reversed potential are presented in Table IV. Total metal content, resin content and glycerin content of the suspensions were varied during these deposition trials. Only suspensions with low metal-to-resin ratio (2.0/1, 2.5/1 and 5.0/1) were used since these had produced the best deposits in the previous deposition trials. Increasing glycerin content has been reported to minimize pitting[7] and glycerin content was also varied for the pulsed-reversed potential deposition trials. The variety of suspension compositions provided a range of resistivities (135 to 360 ohm-cm). The potential was pulsed and reversed such that a complete
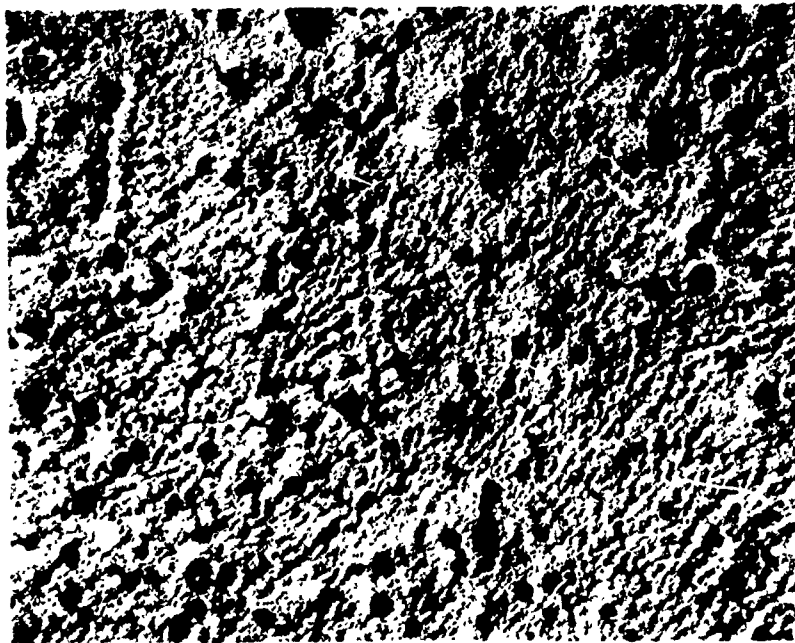
(a) Suspension No. 4
     Ti + V = 10 w/o
     Applied Potential = 100 volts
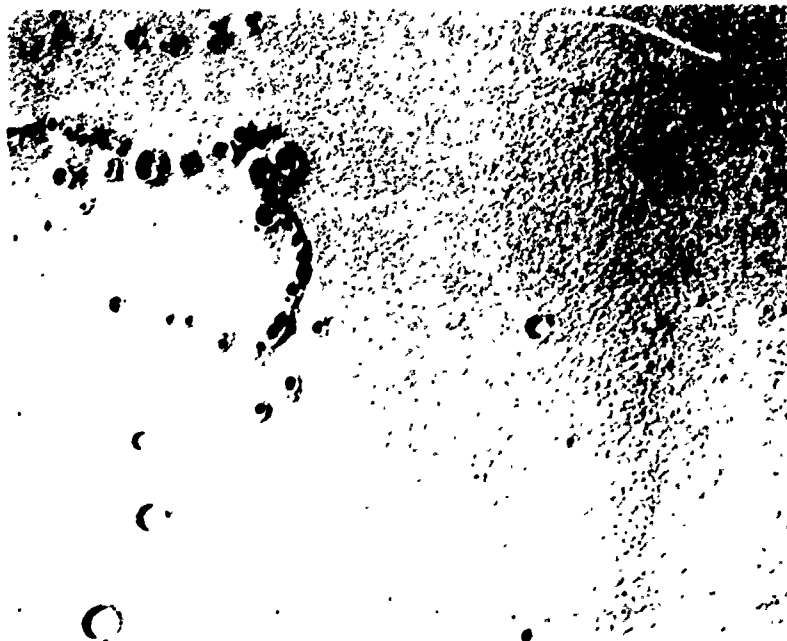
(b) Suspension No. 10
     Ti + V = 20 w/o
     Applied Potential = 70 volts

Figure 3. Examples of Pitting and Streaking Defects Obtained in
           Electrophoretic Deposits from Water Base Suspensions
                                                    (7X mag.)

TABLE IV

EXPERIMENTAL CONDITIONS AND RESULTS OF ELECTROPHORETIC DEPOSITION TRIALS USING A PULSED REVERSING POTENTIAL

| Suspension Composition(a) | | | | | | | Deposition Parameters | | | | | | |
Metal w/o	Ti + Y w/o(b)	Resin w/o	Glycerin w/o	Metal/Resin Ratio	pH	Resistivity (ohm-cm)	Deposition Potential Volts	Deposition Potential Pulse Duration (secs)	Repulsion Potential Volts	Repulsion Potential Pulse Duration (secs)	Total Time (secs)	Wt. Gain (mg/cm²(c))	Comment.
15	10	3.0	2.5	5/1	8.1	135	30	0.33	1.0	0.33	60	-	Uniform Coverage,Few Small Pits
							40					-	" " " "
							50					-	" " " "
							60					-	" " " "
							75		2.0			-	" " " "
							100					25	" " " "
							50		3.0			-	" " " "
							75					-	Uniform Coverage,Increased Pitting
							100	0.17	3.0	0.50		6.1	Uniform Cov., Few Small Pits
							50	0.17	1.0	0.50		-	" " " "
							75	0.50	1.0	0.17		21.7	Uniform Cov., Increased Pitting
							50	0.50	1.0	0.17		34.2	" " " "
15	10	3.0	3.5	5/1	8.0	165	50	0.50	1.5	0.17		-	Uniform Cov.,Pitting&Streaking
							75	0.50	1.5	0.17		-	" " "
							50	0.17	1.5	0.50			Uniform Cov.,Small Pits &
							75		1.5	0.50			" " " Streaks
5	10	2.5	2.5	2.0/1	8.3	320	30	0.50	1.0	0.17		-	Streaks, Small Pits
							50	0.50	1.0	0.17		-	" " "

TABLE IV(continued)

| Suspension Composition(a) | | | | | | | Deposition Parameters | | | | | | |
| Metal w/o | Ti + V w/o(b) | Resin w/o | Glycerin w/o | Metal/Resin Ratio | pH | Resistivity (ohm-cm) | Deposition Potential | | Repulsion Potential | | Total Time (secs) | Wt. Gain (mg/cm²)(c) | Comments |
							Volts	Pulse Duration (secs)	Volts	Pulse Duration (secs)			
5	10	2.0	2.5	2.5/1	8.3	320	30 50 70	0.17 →	1.0 →	0.50	60	– – –	Streaking Streaking Increased Streaking
10	10	2.0	2.0	5/1	7.9	360	50 75 100	0.17 →	1.0 →	0.50 →	→	– – –	Incomplete Coverage Streaking Streaking

NOTES: (a) Balance of suspension was de-ionized water to which 0.001 w/o Orvus was added.

(b) For Ti + V = 10 the metal composition was 25.7 Mo - 64.3 W - 5 Ti - 5 V.

(c) Weight Gain after washing and drying (1 hr/200°F).

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cycle consisted of a deposition pulse (specimen positive) and a repulsion pulse (specimen negative). Vigorous agitation was also used to assist in removal of gas bubbles in the vicinity of the specimen. Deposition potentials were varied from 30 to 100 volts, while the repulsion potential was varied from 1.0 to 3.0 volts. The repulsion potential was maintained at low values to prevent electrolysis in the opposite direction. The times for both the deposition pulse and the repulsion pulse were varied from 0.17 to 0.50 seconds. Variations of the pulses included trials in which the duration of the deposition and repulsion pulses were equal, trials in which the deposition pulse was greater and trials in which the repulsion pulse was greater. The total time for all depositon trials was 60 seconds.

All of the suspension and voltage variations produced pitting or pitting and streaking in the deposits to varying extents. The lowest incidence of defects was obtained in deposits made from suspension No. 12. This suspension produced only a few small pits over a range of deposition potentials (30 to 100 volts) and repulsion potential of either 1.0 or 2.0 volts at equivalent pulse durations of 0.33 seconds. Increasing the repulsion potential to 3.0 volts or the duration of the deposition pulse to 0.50 seconds increased pitting. Typical deposits obtained by pulsing and reversing the applied potential are shown in Figure 4. Figure 4(a) shows a deposit made from suspension No. 12 using a deposition potential of 100 volts and a repulsion potential of 2 volts. The composition of suspension No. 12 was identical to that of suspension No. 4. Comparison of Figure 4(a) with Figure 3(a), which shows a deposit made from suspension No. 4 using a constant applied potential of 100 volts, indicates a drastic reduction in the number and size of pits obtained by the pulsed-reversed potential technique. Figure 4(b) shows a deposit made from suspension No. 12 with a deposition potential of 75 volts and a repulsion potential of 2 volts. Some reduction in the amount and size of pits and streaks is evident in the deposit.

The deposition trials using the pulsed-reversed potential technique demonstrated that pitting and streaking could be minimized but not completely eliminated in deposits made from waterbase suspension. The configuration of the intended application, gas turbine vanes, has both re-entrant angles and internal cavities that would tend to entrap the evolved gas. It was anticipated that the

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(a) Suspension No. 12
Ti + V = 10 w/o
Applied Deposition Potential = 100 volts
Applied Reversed Potential   =   2 volts
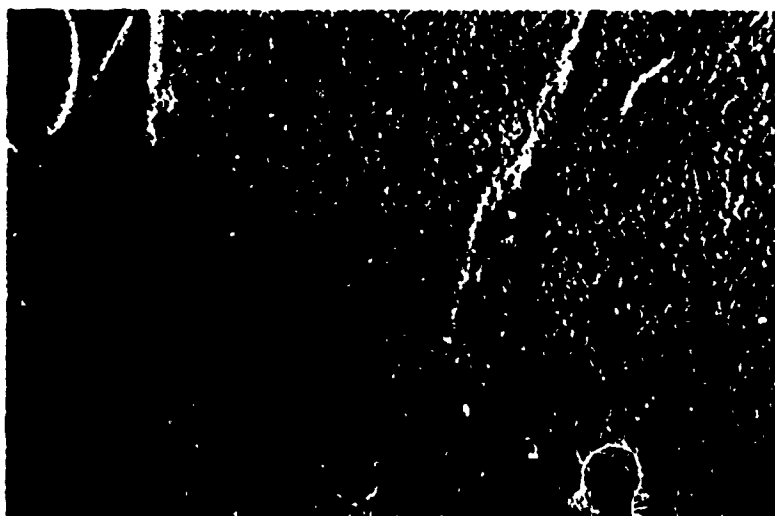
(b) Suspension No. 12
Ti + V = 10 w/o
Applied Deposition Potential = 75 volts
Applied Reversed Potential   = 1.0 volt

Figure 4.   Examples of Electrophoretic Deposits Made from a
Water Base Suspension Using a Pulsed-Reversed Potential
(7X mag.)

problem of pits and streaks would become more acute in depositing the modifier layer on gas turbine vanes from waterbase suspensions. Therefore, modifier layer deposition trials with waterbase suspensions were discontinued and deposition trials were initiated with isoproponol-nitromethane suspensions.

3.2.3   Isoproponol-Nitromethane Suspensions

3.2.3.1   Procedure

Electrophoretic deposits were made from suspensions containing elemental metal powders (W, Mo, Ti and V), zein, cobalteous nitrate, isoproponol and nitro-methane. Suspension volumes of approximately 825 ml were used to determine parameters for depositing the modifier layer. The following procedure was used to mix these suspensions. First a stock solution was made by dissolving 200 grams of zein in a mixture consisting of 275 ml of nitromethane and 575 ml of isopro-ponol. Individual suspensions were then made by dissolving 15 ml of the stock solution in a mixture of 275 ml of nitromethane and 525 ml of isoproponol. The stock solution was dissolved in the isoproponol-nitromethane mixture over a time period of four hours. After filtering, 120 mg of cobalteous nitrate and 42 grams of metal powder were added to the suspension. The metal powder was one of three compositions: 64.3 w/o W + 25.7 w/o Mo + 5 w/o Ti + 5 w/o V (Ti+V = 10), 57.1 w/o W + 22.9 w/o Mo + 10 w/o Ti + 10 w/o V (Ti+V = 20) or 50 w/o W + 20 w/o Mo + 15 w/o Ti + 15 w/o V (Ti+V = 30). The areas where the electrode gripped the specimen were patched with a mixture of nitrocellulose and the appropriate metal powder composition. After deposition parameters had been determined with the 825 ml suspensions, 8 l suspensions were used to deposit the modifier layer on coupons for siliciding trials and oxidation tests and on bend test specimens. The procedure for mixing the 8 l suspensions was the same as described above, except that the amount of each constituent was increased proportionately.

Suspensions were held in beakers and agitated with a magnetic stirrer during deposition trials. Applied potentials were provided by a DC power supply For the isoproponol-nitromethane suspensions, specimen polarity was negative. A conforming anode (positive polarity) consisting of a screen with a rectangular cross section of 0.75 inch x 1.75 inches surrounded the specimen. Polarity of the applied potential was constant during deposition. During the deposition

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trials the potential was varied over the range of 150 to 350 volts. Deposition time varied from 5 to 60 seconds. After deposition the specimens were taken from the suspension and air dried, i.e., the deposits were not rinsed.

Air dried specimens were sintered in a carbon element resistance heated furnace at a vacuum of 10^{-4} to 10^{-5} mm Hg. The specimens were held in boxes fabricated from a columbium alloy. Tungsten rods supported the specimens within the boxes. Sintering time was 15 hours at temperatures of $2760^{\circ}F$, $2830^{\circ}F$ or $2940^{\circ}F$. After sintering the specimens were brushed lightly to remove any unsintered particles.

3.2.3.2 Results

The objective of the electrophoretic development was to determine deposition parameters (applied potential and deposition time) that would produce sintered modifier layer thicknesses of 2.0, 3.5 and 5.0 mils for each of the modifier layer compositions. In addition, it was desirable to determine thickness of the sintered modifier layer as a function of the as-deposited specimen weight gain. This latter relationship would then serve as a control for suspension depletion with scale-up to larger volume suspensions.

All of the electrophoretic parameter development work was done with 20 mil FS-85 sheet. Preliminary deposition trials were made with a suspension containing a total Ti+V content of 10 w/o to determine the voltage range where deposits could be obtained and a rough estimate of the relationship between specimen weight gain and modifier layer thickness. Deposits were made on a series of specimens using a variety of applied potentials and deposition times to obtain a wide range of specimen weight gains. Specimen weight gain was determined after air drying. Modifier layer thickness was then determined by micrometer measurements. Results of the preliminary deposition trials are presented in Table V. Deposits were made on a total of 36 specimens. Both suspension pH and resistivity decreased as deposits were made from the suspension. The initial suspension ph of 3.1 decreased to 2.7 after deposits had been made on 17 specimens and to 2.6 after deposits had been made on 35 specimens. During the same intervals suspension resistivity decreased from an initial value of 5450 ohm-cm to 4800 ohm-cm and 4000 ohm-cm. Specimen weight gains ranged from 10.4 mg/cm^2 to 68.6 mg/cm^2

TABLE V

RESULTS OF PRELIMINARY ELECTROPHORETIC DEPOSITION TRIALS WITH ISOPROPONOL NITROMETHANE SUSPENSIONS

Ti+V Content w/o(a)	Specimen No.	ph(b)	Resistivity (ohm-cm) (b)	Deposition Parameters Potential (volts)	Time (sec)	Weight Gain mg/cm²	Thickness (mils) Micrometer(c)
10	1	3.1	5450	350	10	27.9	3.6
	2	-	-	"	20	58.7	6.6
	3	-	-	"	30	68.6	8.05
	4	-	-	250	10	20.2	2.8
	5	-	-	"	20	38.4	4.35
	6	-	-	"	30	53.9	5.75
	7	-	-	150	10	10.4	1.85
	8	-	-	"	20	19.1	2.6
	9	-	-	"	30	27.7	3.1
	10	-	-	350	10	31.6	3.8
	11	-	-	"	20	55.4	6.1
	12	-	-	"	30	80.6	7.85
	13	-	-	250	10	10.8	2.65
	14	-	-	"	20	38.3	4.2
	15	-	-	"	30	56.0	6.0
	16	-	-	150	10	11.3	1.95
	17	-	-	"	20	19.2	2.45
	18	2.7	4800	"	30	29.6	3.3
	19	-	-	350	5	17.7	2.75
	20	-	-	"	10	31.8	3.75
	21	-	-	"	15	43.1	4.7
	22	-	-	250	5	11.4	2.0
	23	-	-	"	10	20 6	2.7
	24	-	-	"	15	30.5	3.75
	25	-	-	150	40	40.9	4.55
	26	-	-	"	50	46.0	4.9
	27	-	-	"	60	50.0	5.15
	28	-	-	350	5	17.1	2.55
	29	-	-	"	10	26.1	3.5
	30	-	-	"	15	41 7	4.75
	31	-	-	250	5	11.0	2.1
	32	-	-	"	10	20.7	2.8
	33	-	-	"	15	28 6	3.5
	34	-	-	150	40	37.0	3.9
	35	-	-	"	50	44.8	4.6
	36	2.6	4000	"	60	41.1	4.8

NOTES: (a) Metal Composition - 25.7 Mo - 64.3 W - 5Ti-5V
      (b) pH and resistivity were measure prior to deposition of coating for certain selected trials.
      (c) Micrometer measurements after air drying
      (d) Metallographic measurements after sintering 15 hrs/2760°F in a 10^{-3} mmHg vacuum.

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with micrometer measurements indicating that modifier layer thicknesses of from 1.85 to 8.05 mils were deposited on the specimens.

After the preliminary deposition trials, a second series of deposition trials was conducted using all three metal powder compositions and a variety of applied potentials and deposition times. Weight gains of the air dried specimens were determined and then the specimens were sintered at $2760^{\circ}F$ or $2940^{\circ}F$. Selected specimens were then examined metallographically to determine the sintered modifier layer thickness. Based on the results of the preliminary deposition trials, specimens with air-dried weight gains within the range of 12.6 to 66.0 mg/cm^2 were selected for the metallographic examination. Measurements of the modifier layer thickness were made on the sides, edges and corners of the specimens as shown in Figure 5.

Thicknesses of the modifier layers are tabulated in Table VI along with weight gains, sintering temperatures and deposition parameters. Average modifier layer thicknesses for the sides, edges and corners as well as ranges for these locations are tabulated in Table VI. The same data are plotted in Figures 6, 7 and 8 as a function of weight gain. Average modifier layer thicknesses on the sides of the specimens ranged from 1.05 to 6.13 mils. Thickness variations (the difference between the lowest and highest values) in this location on individual specimens ranged from 1.0 to 2.75 mils with the majority of the specimens having variations in the 1.0 to 2.0 mil range. The larger variations were associated with the heavier modifier layer thicknesses. Thickness variations on edges were dependent on the modifier layer thickness on the sides of the specimens. Specimens with an average modifier layer thickness on the sides of 2 mils or less had equivalent or somewhat heavier layers on the edges. In general, specimens with an average modifier layer thickness on the sides of greater than 2 mils had thinner layers on the edges. This reduction in thickness ranged from 0.25 to 2.0 mils on individual specimens, with the majority of the specimens having less than a 1.0 mil average thickness difference between the sides and edges. Average modifier layer thicknesses on the corners of all specimens were less than the average thicknesses on the sides of the specimens. The reduction in thickness between sides and corners ranged from 0.25 mils for the thinner layers to as much as 3.0 mils for the thicker layers. In general, corners and edges had

26
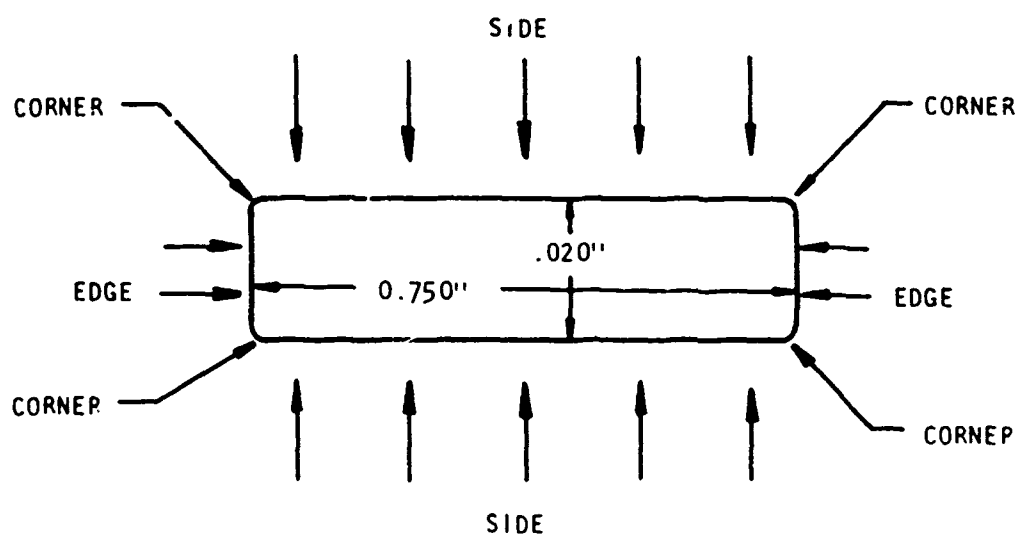
Figure 5. Locations of Metallographic Measurements of Modifier Layer Thickness.

TABLE VI

THICKNESS OF MODIFIER LAYERS DEPOSITED ON FS-85 COLUMBIUM ALLOY

Ti+V Content w/o	Sintering Temp. °F	Specimen No.	Deposition Parameters Potential Volts	Deposition Parameters Time Sec.	Wt(d) Gain mg/cm²	Sides Avg.	Sides Range	Edges Avg.	Edges Range	Corners Avg.	Corners Range
10(..)	2760	A56	150	10	12.6	1.05	.75/2.0	1.13	0.5/1.75	0.88	0.5/1.5
		A8	150	20	18.1	1.75	1.25/2.25	1.88	1.0/2.75	1.25	0.5/2.25
		A9	150	30	25.9	2.38	1.5/3.5	2.40	1.75/3.0	1.75	1.25/2.25
		A59	250	30	53.7	5.08	4.0/6.75	4.38	1.75/6.25	4.13	2.0/5.0
		A54	350	20	62.2	6.2	4.5/8.0	5.75	4.5/7.5	3.75	2.5/5.75
10(a)	2940	A10	350	5	17.0	1.28	1.0/2.0	2.0	1.25/2.5	1.25	0.75/2.0
		A1	350	10	30.6	2.43	1.75/3.0	3.44	3.25/3.75	2.0	1.5/2.75
		A5	250	20	37.4	3.35	2.75/4.0	4.13	3.5/4.75	2.68	2.0/3.0
		A6	250	30	54.9	4.35	3.0/5.5	5.25	4.5/5.5	2.87	1.75/3.5
20(b)	2940	A78	250	5	9.0	1.05	0.5/1.5	1.12	1.0/1.25	0.87	0.75/1.0
		A74	350	5	14.5	1.53	1.0/2.0	1.68	1.5/2.25	1.12	0.5/1.75
		A95	'50	30	18.9	1.70	1.25/2.50	1.80	1.25/2.25	1.68	0.5/2.5
		A86	350	10	25.7	2.40	1.50/3.75	2.63	2.5/3.0	1.37	0.5/2.0
		A81	250	30	41.0	3.68	2.75/4.25	1.63	0.75/2.25	2.5	0.5/4.5
		A76	350	20	51.1	4.2	2.75/5.75	4.25	3.5/5.0	1.05	0.5/3.75
		A77	350	30	63.0	5.67	4.75/7.50	4.5	3.5/5.75	3.70	2.75/5.5
30(c)	2940	A96	350	5	15.3	1.45	1.0/2.0	2.12	1.75/2.75	1.25	0.5/1.75
		A112	350	10	24.9	2.25	1.25/3.0	2.63	2.0/3.0	1.75	1.25/2.25
		A114	350	15	34.3	3.18	2.5/4.0	2.87	2.5/3.75	1.88	1.25/3.0
		A103	250	30	44.8	4.4	3.0/5.75	4.25	3.0/5.5	2.75	2.0/3.5
		A104	250	40	53.9	4.8	3.25/5.5	4.13	2.5/4.75	2.56	0.75/3.75
		A100	350	30	66.1	6.13	5.0/7.0	4.55	2.25/6.75	3.0	1.0/5.0

TABLE VI (continued)

NOTES:

(a) Ti+V = 10 w/o
Powder Composition = 25.7Mo-64.3W-5Ti-5V
Initial pH - 3.7
Initial Resistivity : 8500 ohm-cm

(b) Ti+V = 20 w/o
Powder Composition = 22.9Mo-57.1W-10Ti-10V
Initial pH = 3.4
Initial Resistivity = 6700 ohm-cm

(c) Ti+V = 30 w/o
Powder Composition = 20Mo-50W-15Ti-15V
Initial pH = 3.0
Initial Resistivity = 6150 ohm-cm

(d) Weight Gain after Air Drying

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Figure 6. Modifier Layer Thickness on Sides, Edges and Corners of Specimens as a Function of Weight Gain for Specimens Coated from Suspensions Containing Ti + V Contents of 10 w/o and Sintered at 2760°F or 2940°F.

Figure 7. Modifier Layer Thickness on Sides, Edges and Corners of Specimens as a Function of Weight Gain for Specimens Coated from Suspensions Containing Ti + V Contents of 20 w/o and Sintered at 2940°F.
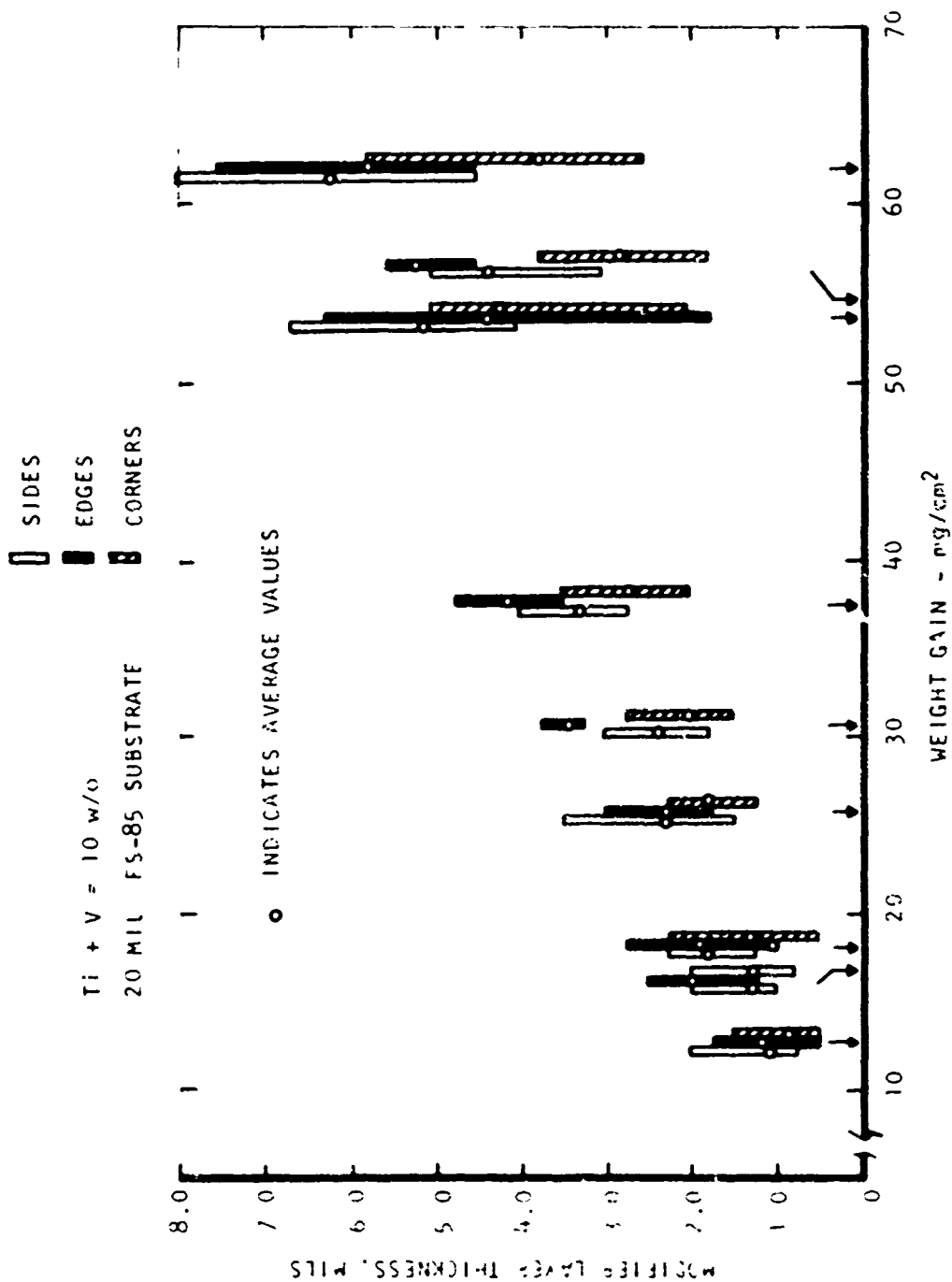
31

Figure 8. Modifier Layer Thickness on Sides, Edges and Corners of Specimens as a Function of Weight Gain for Specimens Coated from Suspensions Containing Ti + V Contents of 30 w/o and Sintered at 2940°F.

greater thickness variations on individual specimens than sides of the specimens.
Thic'ness uniformity on corners and edges of the specimens was strongly dependent
on the configuration of the sheared edges of the specimen. Edges sheared perpen-
dicular to the sides provided more uniformity than edges that were not perpendicular
to the sides of the specimen. This dependence on substrate configuration is
illustrated in Figure 9. The edges of specimens prepared later in the program
were surface ground prior to tumbling in order to provide a better substrate con-
figuration. Some variation in modifier layer thickness can also be attributed to
handling, incomplete sintering and edge retention during metallographic preparation
In the air dried condition, the coatings were somewhat powdery resulting in some
loss during handling. In addition, particles that were not adherent after sinter-
ing were removed by brushing.

Plots of the average modifier layer thicknesses on the sides of the
specimens are shown in Figures 10, 11 and 12 for deposits made from suspensions
containing Ti+V contents of 10 w/o, 20 w/o and 30 w/o, respectively. The plot
for the suspension with a Ti+V content of 10 w/o differentiates between specimens
sintered at 2760°F and specimens sintered at 2940°F. This plot indicates that
there was no difference in modifier layer thicknesses between specimens sintered
at 2760°F and specimens sintered at 2940°F. The higher sintering temperature
apparently did not result in more complete sintering or significantly higher
vaporization losses of the modifier layer elements. Specimens with deposits made
from suspensions containing total Ti+V contents of 20 and 30 w/o were sintered
only at 2940°F. Using the plots in Figures 10, 11 and 12, weight gain ranges were
selected for producing nominal modifier layer chemistry variations. These weight
gain ranges are shown in Table VII. In general, increasing the Ti+V content of
the suspension required a lower weight gain to produce a given modifier layer
thickness.

Microstructures of nominal 3.5 and 5.0 mil thick sintered modifier layers
are presented in Figure 13. The microstructures show the porous nature of the
sintered modifier layers. Microstructures and electron microprobe X-ray rasters
of nominal 2 mil thick sintered modifier layers deposited from the three suspension
compositional variations are shown in Figures 14 through 19. The electron micro-
probe X-ray rasters give a qualitative indication of the distribution of the

23
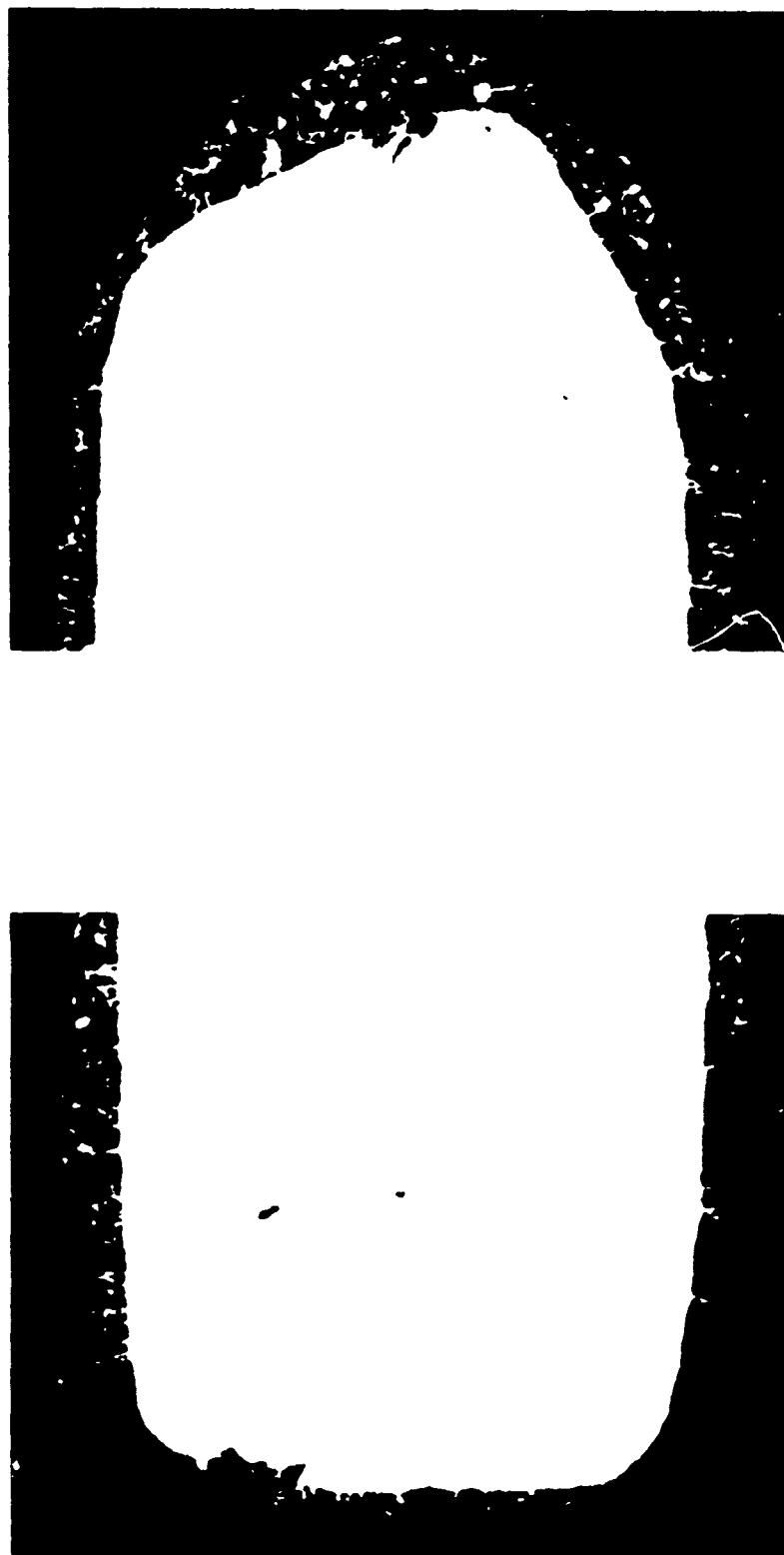
Figure 9. Sintered Modifier Layer on Specimen A112, Showing the Effect of Substrate Edge Configuration on Thickness Uniformity. (Unetched, 160X mag.)
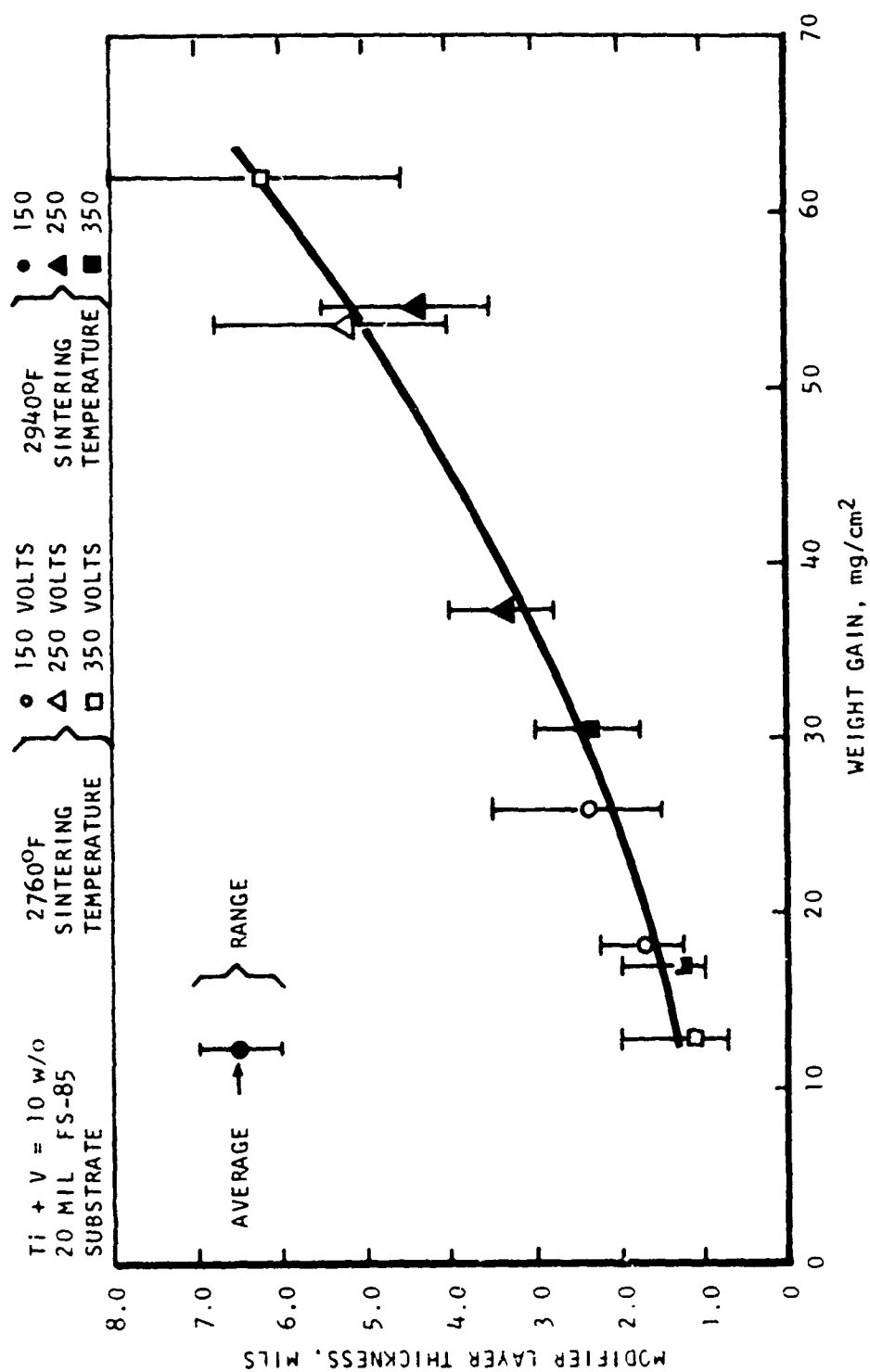
Figure 10. Modifier Layer Thickness on Sides of Specimens as a Function of Weight Gain for Specimens Coated from Suspensions Containing Ti + V Contents of 10 w/o and Sintered at 2760°F or 2940°F.
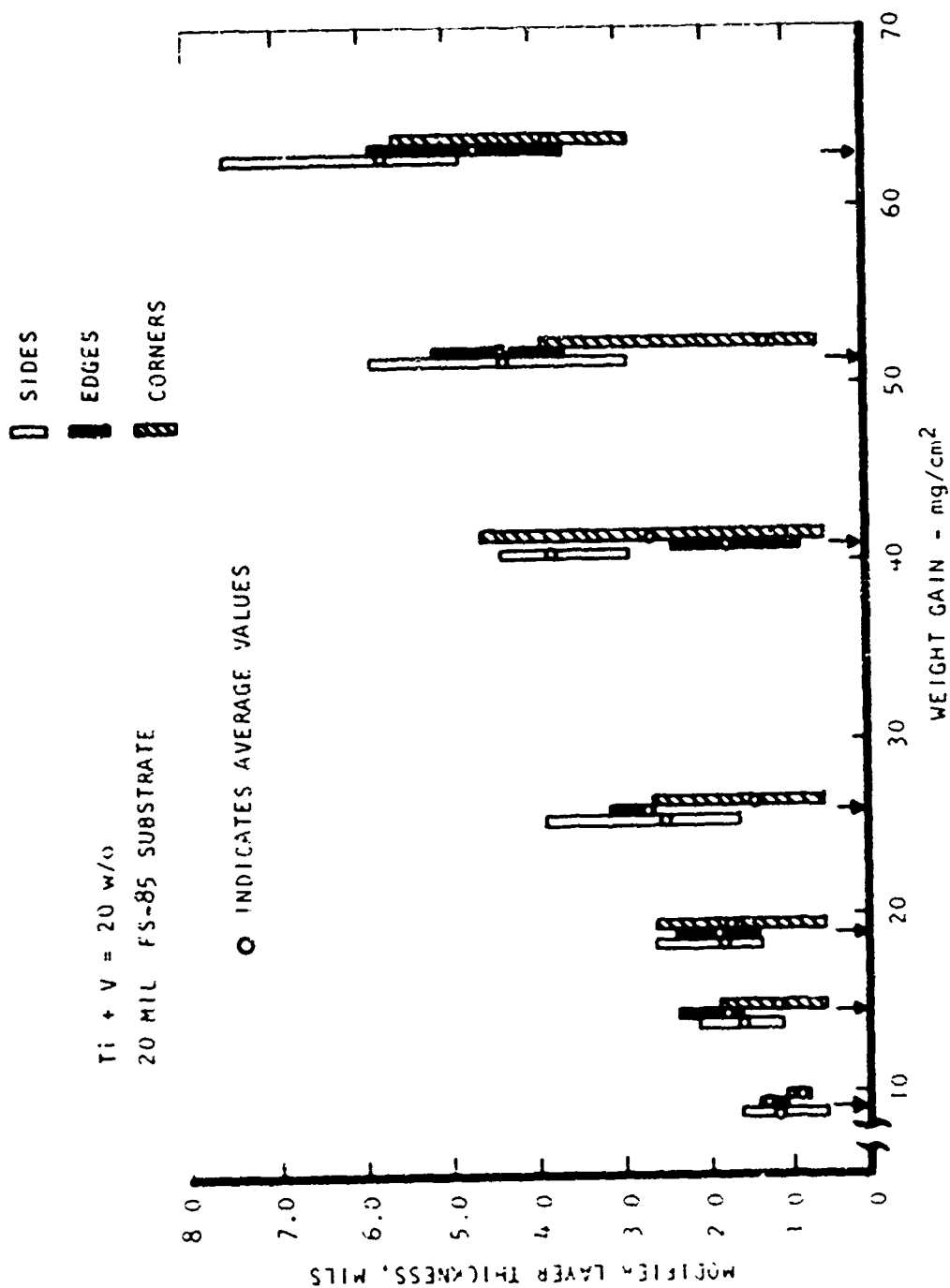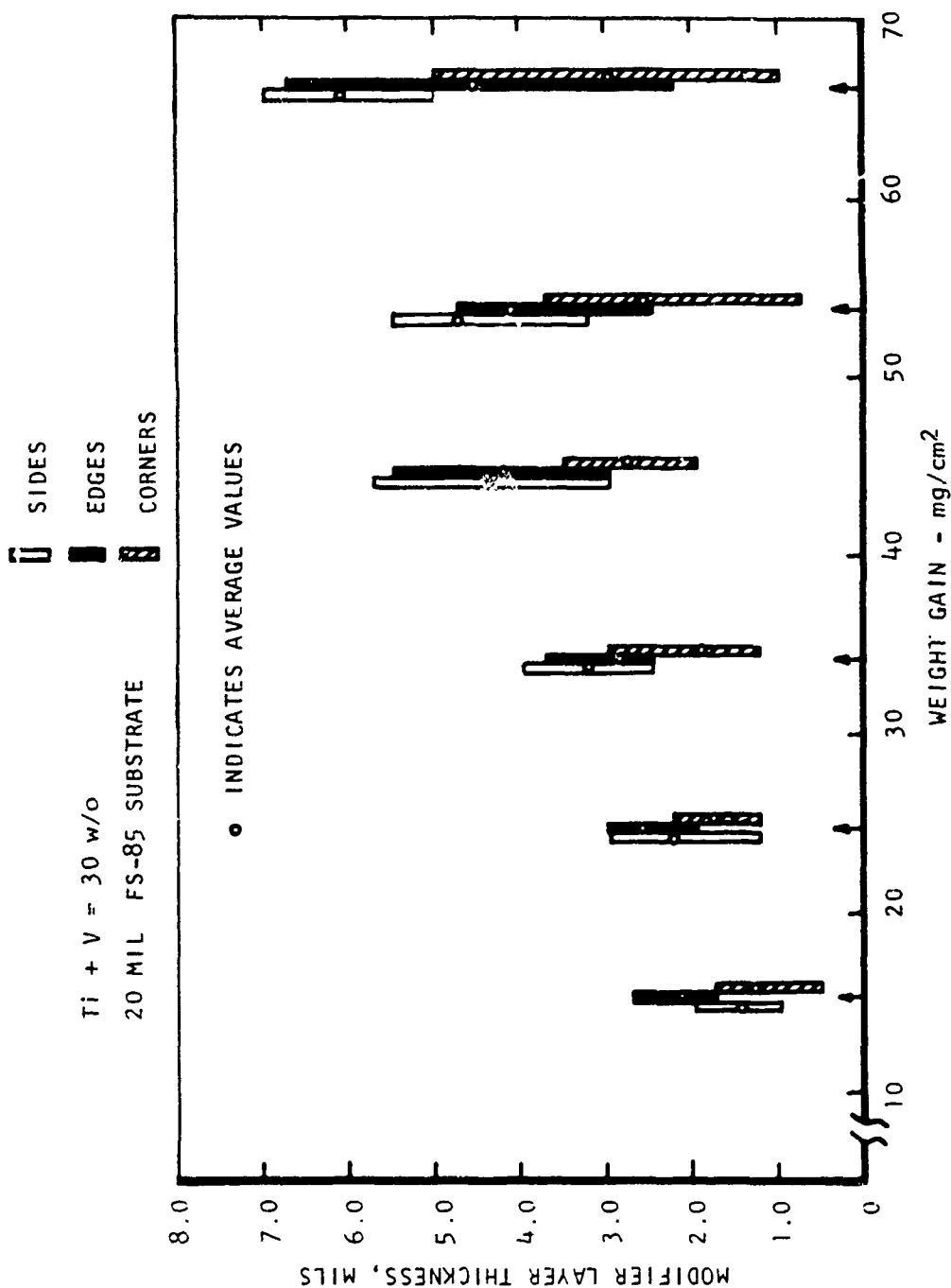
35
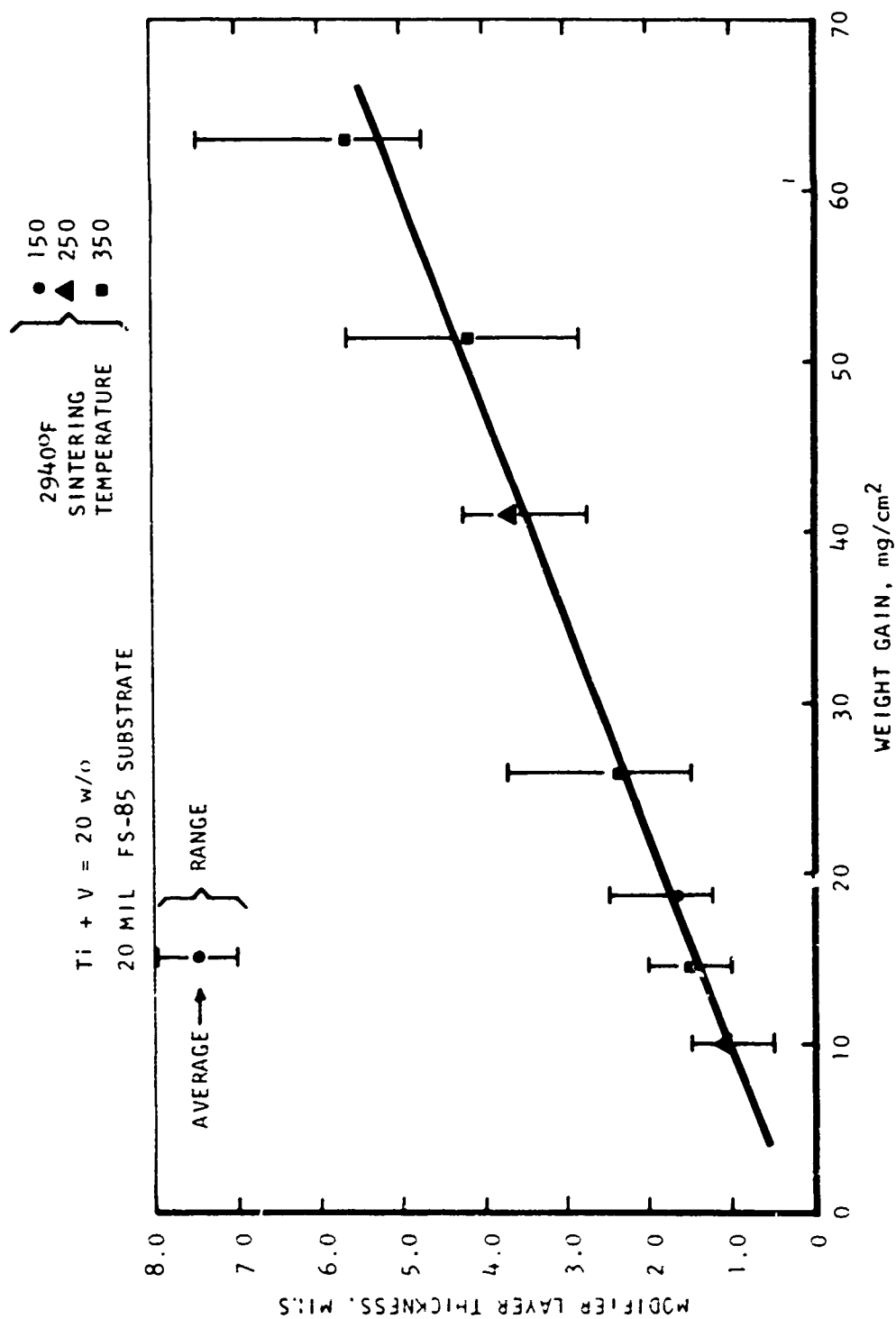
Figure 11. Modifier Layer Thickness on Sides of Specimens as a Function of Weight Gain for Specimens Coated from Suspensions Containing Ti + V Contents of 20 w/o and Sintered at 2940°F.
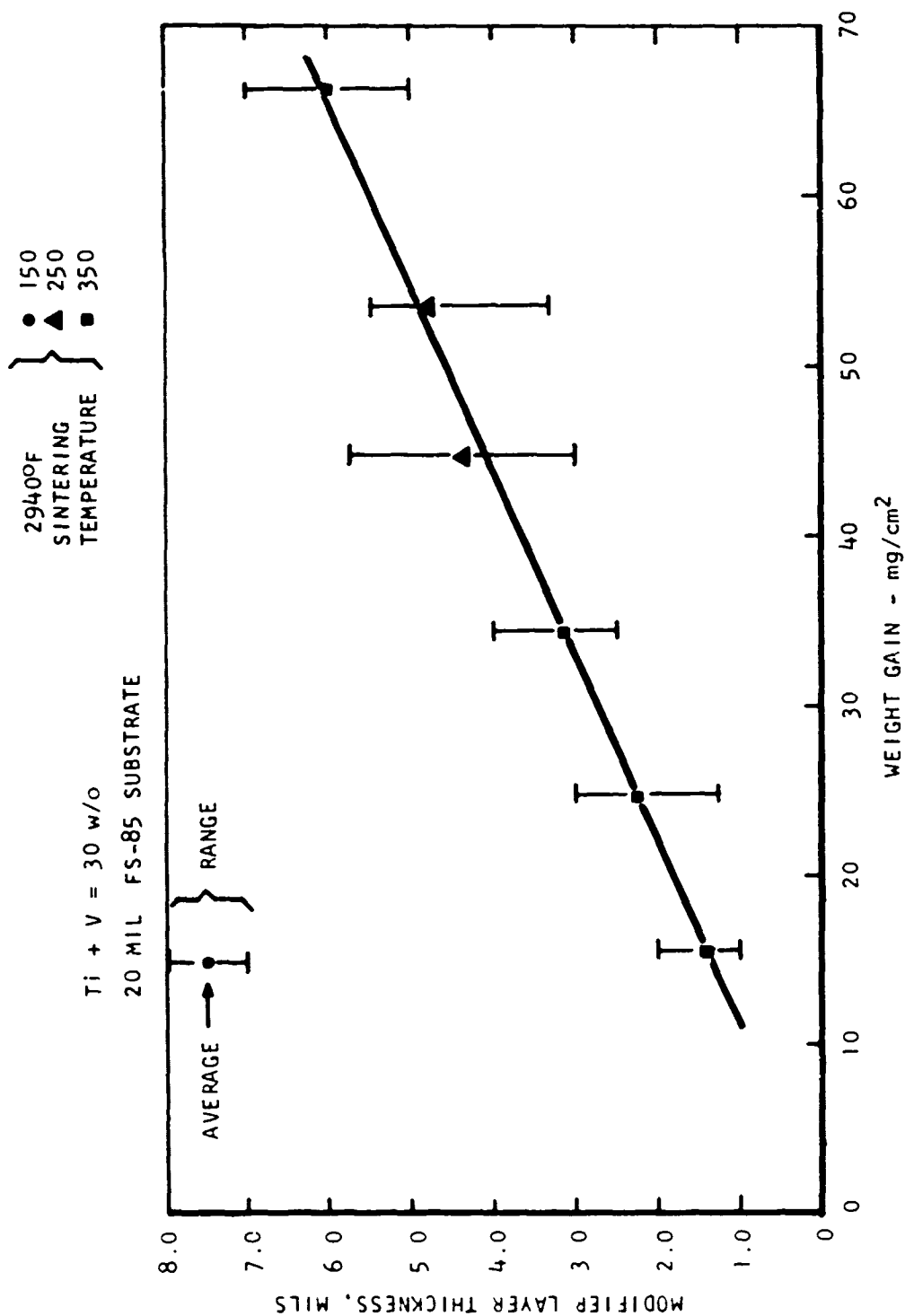
Figure 12. Modifier Layer Thickness on Sides of Specimens as a Function of Weight Gain for Specimens Coated from Suspensions Containing Ti + V Contents of 30 w/o and Sintered at 2940°F.

TABLE VII

WEIGHT GAIN RANGES SELECTED FOR
PRODUCING ELECTROPHORETICALLY DEPOSITED
MODIFIER LAYERS ON FS-85 COLUMBIUM ALLOY

Ti+V Content, w/o	Weight Gain Range for Nominal Modifier Layers Thickness (mg/cm^2)		
	2.0 mils	3.5 mils	5.0 mils
10	22.5-27.5	38.5-43.5	51.0-56.0
20	19.5-24.5	37.5-42.5	55.5-60.5
30	17.5-22.5	33.5-38.5	51.5-56.5
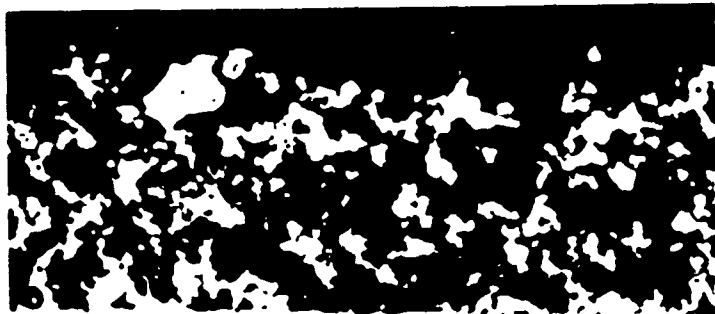
(a) Specimen 20A81
   Average Thickness - 3.68 mils
   Suspension Ti + V Content - 20
   Sintering Temperature - 2940°F
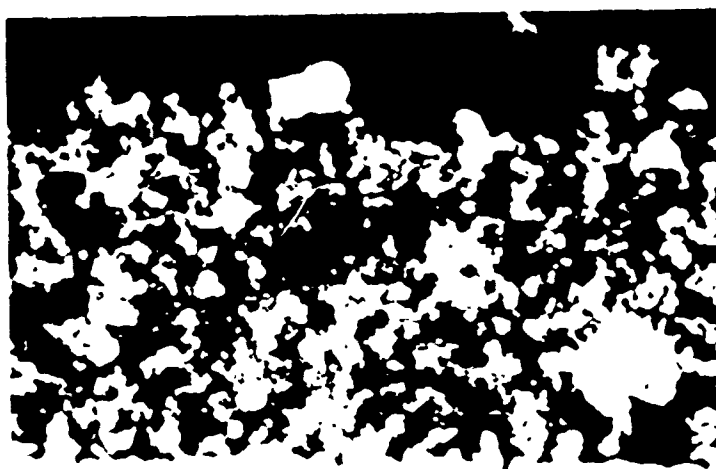
(b) Specimen 20A104
   Average Thickness - 4.8 mils
   Suspension Ti + V Content - 30
   Sintering Temperature - 2940°F

Figure 13. Microstructures of Typical Electrophoretically Deposited
            Modifier Layer After Sintering.

                                        (Unetched, 350X mag.)
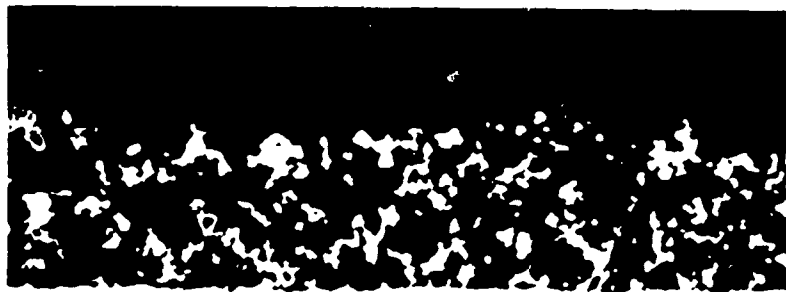
(a)   350X (Unetched)

(b)   400X

Figure 14. (a) Microstructure and (b) Back Scatter X-Ray
            Raster of the Sintered Layer on Specimen 20A9.
                 Average Thickness - 2.38 mils
                 Suspension Ti + V Content - 10 w/o
                 Sintering Temperature - 2760°F

(a) W
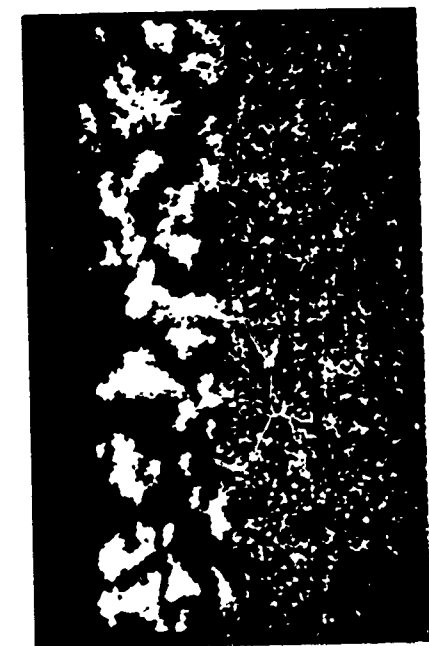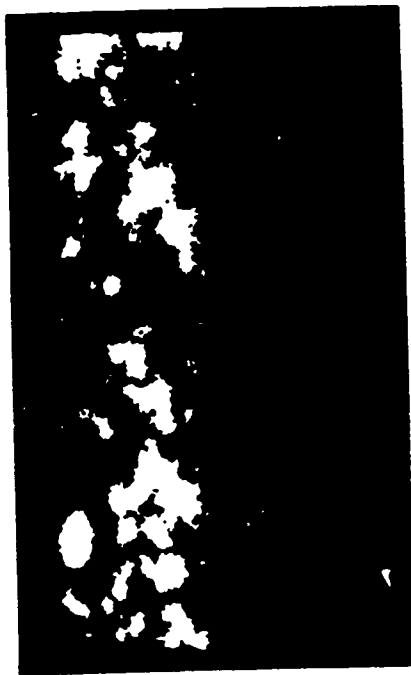
(b) Mo

(c) Ti
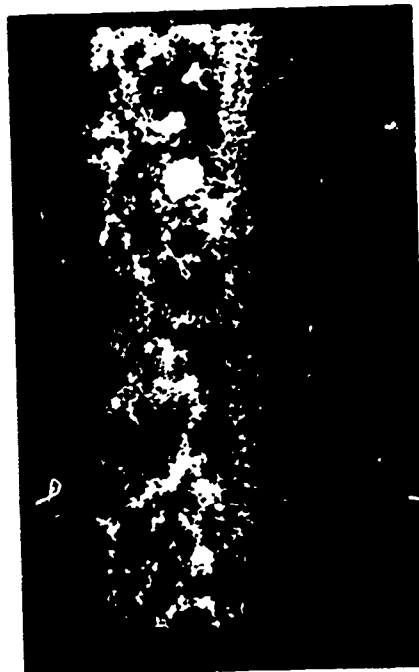
(d) V

Figure 15. Electron Microprobe X-Ray Rasters of Specimen 20A9 (400X)
Average Thickness - 2.38 mils   Suspension Ti + V Content - 10 w/o

(a)   350X (Unetched)
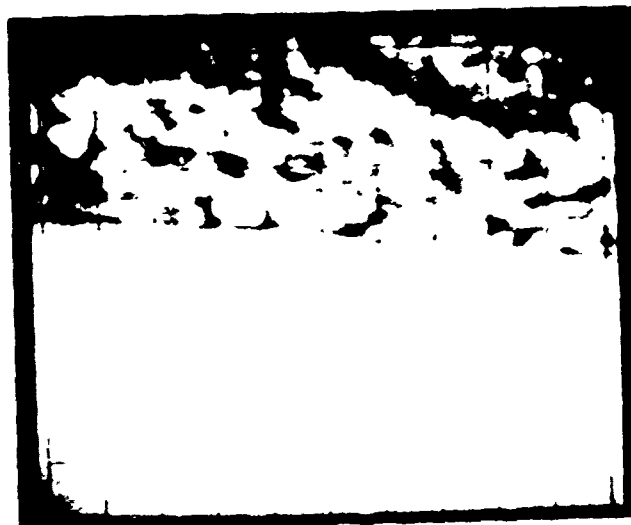
(b)   400X

Figure 16.   (a) Microstructure and (b) Back Scatter X-Ray
Raster of the Sintered Layer on Specimen A86
Average Thickness - 2.40 mils
Suspension Ti + V Content - 20 w/o
Sintering Temperature - 2940°F
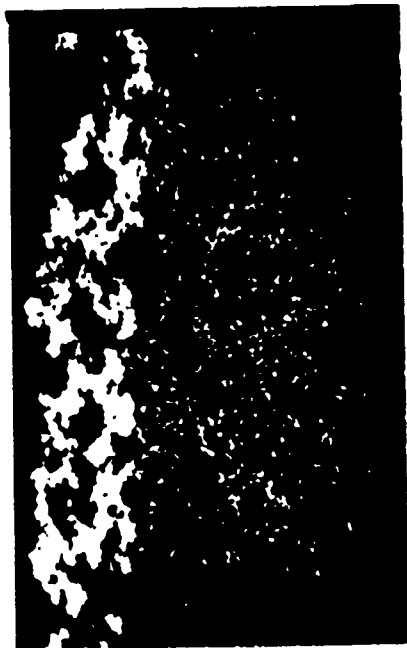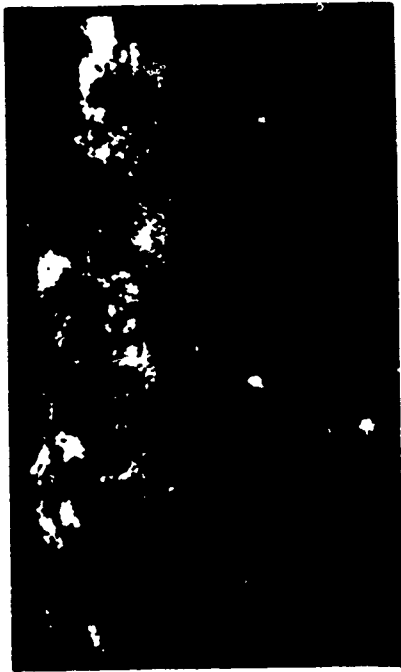
(a) W   (b) Mo
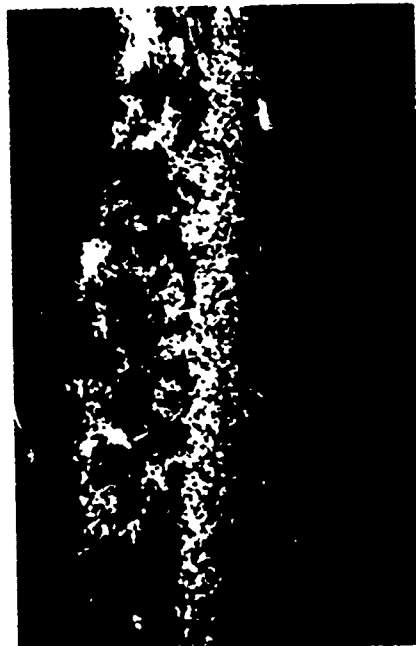
(c) Ti   (d) V

Figure 17.   Electron Microprobe X-Ray Rasters of Specimen 20A86   (400X)
Average Thickness - 2.38 mils   Suspension Ti + V Content - 20 w/o

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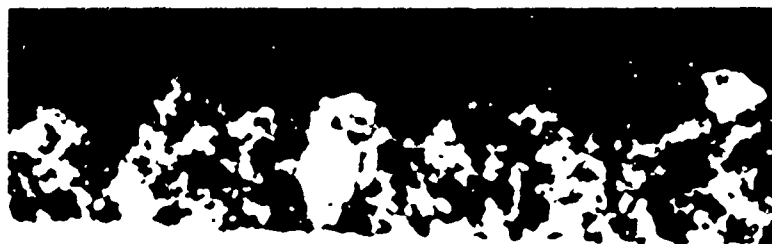
(a)   350X (Unetched)
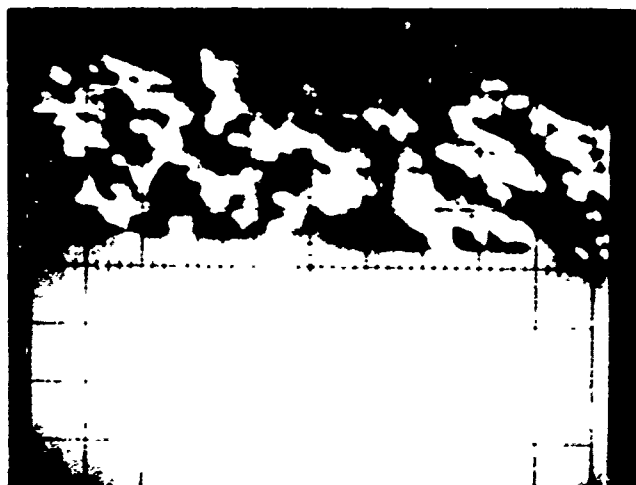
(b)   400X

Figure 18.   (a) Microstructure and (b) Back Scatter X-ray
             Raster of the Sintered Layer on Specimen A112
                   Average Thickness - 2.25 mils
                   Suspension Ti + V Content - 30 w/o
                   Sintering Temperature - 2940°F

(a) W   (b) Mo

(c) Ti   (d) V
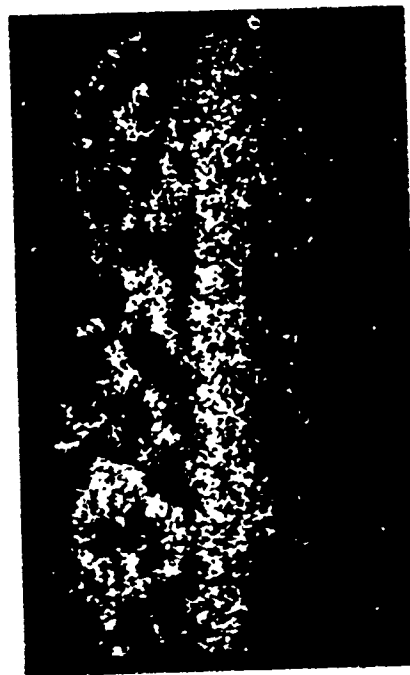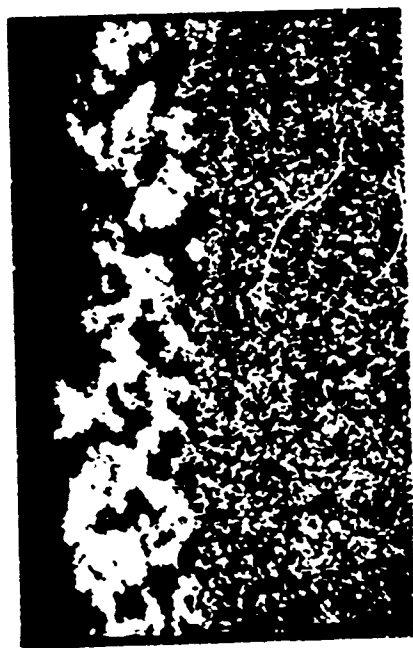
Figure 19. Electron Microprobe X-Ray Rasters of Specimen A112 (400X)
Suspension Ti + V Content - 30 w/o
Average Thickness - 2.25 mils

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elements within the modifier layer and the extent of diffusion into the substrate. Tungsten appeared only in the modifier layers. Molybdenum was contained in the modifier layer of the specimen sintered at $2760^{\circ}F$ (specimen 20A9, Figure 15(b)), but appeared in both the modifier layer and in the adjacent substrate area in specimens sin.ered at $2940^{\circ}F$ (specimens A86 and A112 in Figures 17(b) and 19(b)). Titanium and vanadium had diffused into the substrate in all three of the speci- mens. Although deposited from the electrophoretic suspensions as discrete elementul particles, the elements did not appear as individual particles in the sintered layers. The post-deposition sintering heat treatments were sufficient to crovide some homogenization.

Using electrophoretic deposition parameters developed in this phase of the work and the target gains listed in Table VII, modifier layers were deposited on additional coupons. These coupons were used to develop parameters for depositing silicon on the modifier layers by chemical vapor deposition. This work is described in the next section.

3.3   Development of Chemical Vapor Deposition Parameters

The objective of this phase of the work was to develop chemical vapor deposition (CVD) parameters for depositing silicon on the sintered modifier layers by hydrogen reduction of silicon tetrachloride. Parameters were to be developed for producing silicon to modifier layer atomic ratios of >2.1, 2.5 and 3.0 for all three of the modifier layer chemistry variations (Ti+V = 10, 20 and 30 w/o) at the three modifier layer thickness levels (2.0, 3.5 and 5.0 mils).

3.3.1   Procedure

Silicon was deposited on sintered modifier layers using the pulsed pressure chemical vapor deposition (CVD) equipment shown in Figure 20. A schematic diagram depicting the coating cycle is shown in Figure 21. The major components of the CVD equipment are a $SiCl_4$ chamber where liquid $SiCl_4$ is vaporized, a mixing chamber where H_2 and $SiCl_4$ vapor are mixed, an induction heated reaction chamber where $SiCl_4$ is reduced to Si and a mechanical vacuum pump. The operational sequence of the CVD equipment is as follows: initially, all solenoids are opened with a manual override switch and the entire system is evacuated to a pressure of 0.1 mm Hg. The entire system is then purged by alternately backfilling with argon

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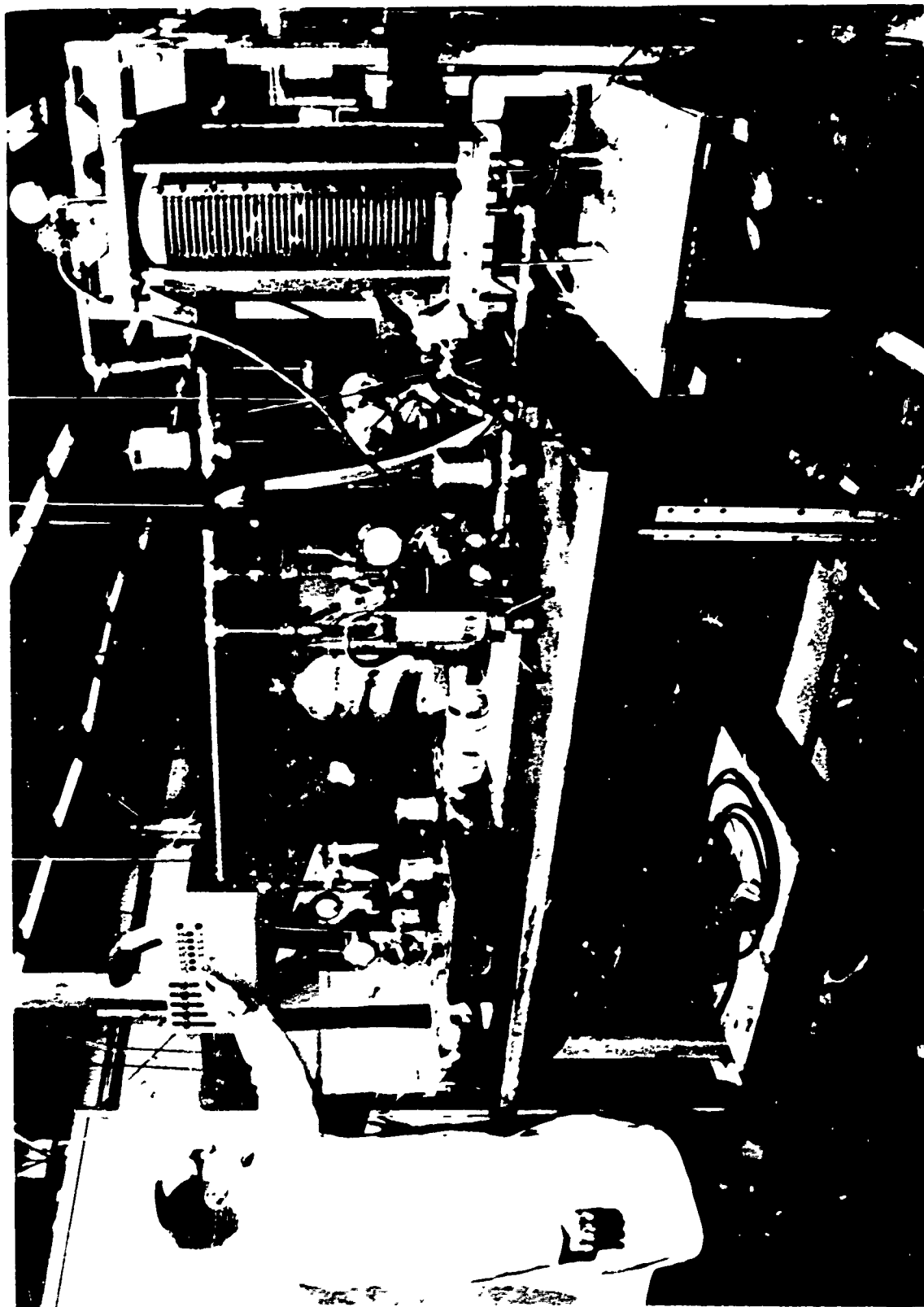
Figure 20. Pulsed Pressure Chemical Vapor Deposition Equipment.

SYMBOLS

⌀ MANUAL VALVE

Ⓙ REGULATOR
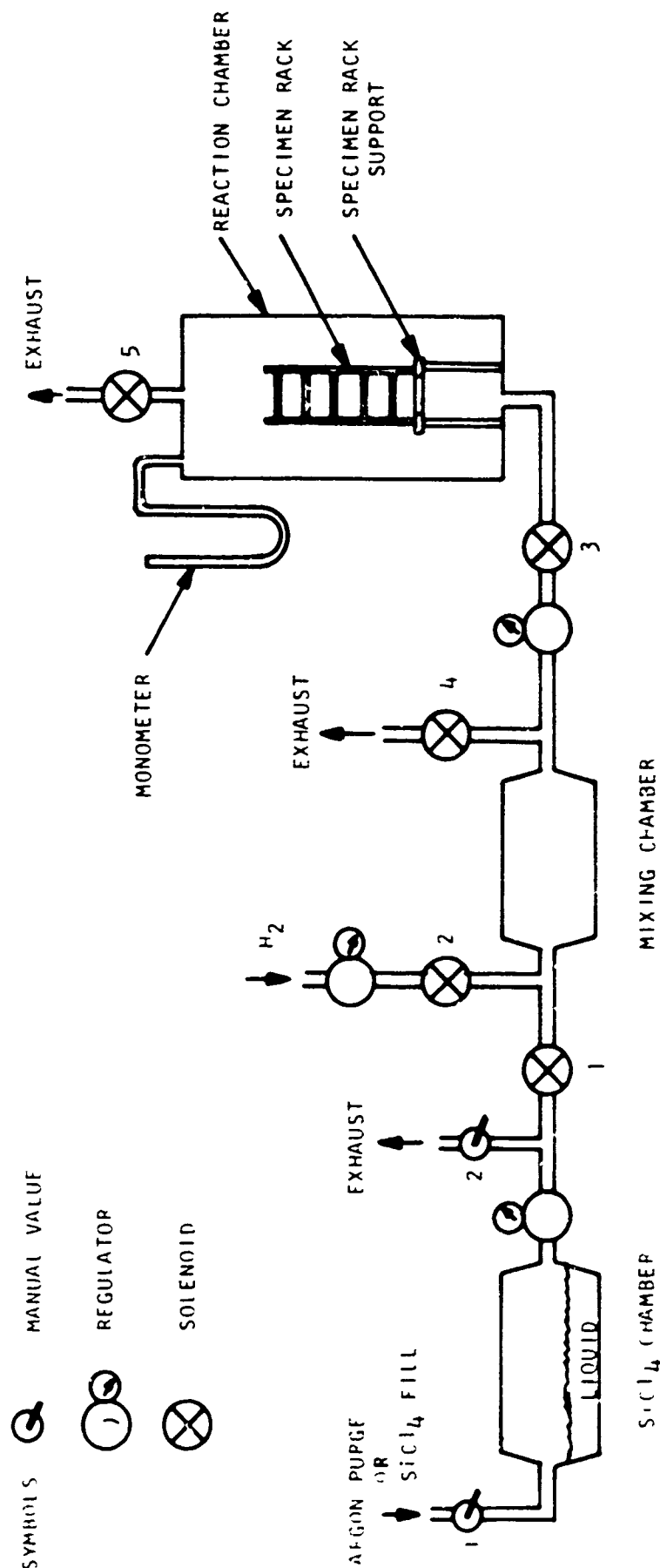
⊗ SOLENOID

OPERATION CYCLE -

A. ADMIT SiCl₄ Gas to Mixing Chamber - Solenoid No. 1 Open, All Other Solenoids Closed.

B. ADMIT H₂ Gas to Mixing Chamber - Solenoid No. 2 Open, All Other Solenoids Closed.

C. ADMIT H₂/SiCl₄ Mixture to Reaction Chamber, Solenoid No. 3 Open, All Other Solenoids Closed.

D. REACT H₂/SiCl₄ Mixture and Evacuate Mixing Chamber - Solenoid No. 4 Open, All Other Solenoids Closed.

E. REMOVE Reactant Gases - Solenoid No. 5 Open, All Other Solenoids Closed.

Figure 21. Schematic Diagram of Pulsed Pressure Chemical Vapor Deposition Equipment.

followed by evacuation. After purging all solenoids are closed, the $SiCl_4$ chamber is then heated to $200^{\circ}F$ to vaporize the $SiCl_4$ and the reaction chamber is heated to the desired reaction temperature. The mixing chamber is also heated to $200^{\circ}F$ to prevent $SiCl_4$ condensation during the coating cycles.

After the desired reaction temperature is reached, the coating cycle is initiated. The coating cycle is automatically controlled by a cyclic timer that opens the solenoids at the appropriate times. The cyclic timer is capable of providing a variety of total time cycles and individual sequence times. For the majority of the deposition runs, the total cycle time was 40 seconds. A total cycle consisted of the follow:..; sequence.

Operation Sequence	Time (Seconds)
A. Admit $SiCl_4$ Gas to Mixing Chamber	4
B. Admit H_2 to Mixing Chamber	4
C. Admit $H_2/SiCl_4$ Mixture to Reaction Chamber	4
D. React $H_2/SiCl_4$ Mixture and Evacuate Mixing Chamber	16
E. Evacuate Reactant Gases from Reaction Chamber	12

The above cycle was repeated as many times as necessary to produce the desired total deposition time. For one deposition run, the reaction time (Step D in the operational sequence) was increased to 36 seconds, making a total cycle time of 60 seconds.

Evacuation of the mixing chamber prior to the initiation of each cycle assures a constant ratio of H_2 to $SiCl_4$. The purpose of the cyclic evacuation of the reaction chamber to remove reaction products and re-introduction of fresh reactant gases is to provide a uniform coating thickness on complex configurations. Cyclic removal of the reaction products allows all surfaces to be contacted by fresh reactant gases and eliminates the flow patterns characteristics of continuous chemical vapor deposition processes.

Regulators were used to control the amounts of $SiCl_4$ and H_2 admitted to the mixing chamber and the amount of $H_2/SiCl_4$ mixture that was admitted into the reaction chamber. Mechanical gages were used to monitor the $SiCl_4$ chamber pressure and pressure in the mixing chamber. A mechanical gage was used to continuously monitor the pressure within the reaction chamber. The mechanical

gage was calibrated with a manometer prior to the initiation of each deposition cycle.

Specimens were supported in the reaction chamber by a rack made from columbium with tungsten pins to hold the specimens. Semi-conductor grade $SiCl_4$ (Airco Products) and technical grade hydrogen were used as the reactant gases. The hydrogen was passed through a Redox unit and a titanium chip heater prior to introduction into the mixing chamber.

Silicon pickup by the modifier layers was calculated on the basis of the atomic ratio of silicon to modifier layer elements using the following relation:

$$\frac{Si}{Mod.\ Elements} = \frac{\dfrac{Wt_{Si}}{At\ Wt_{Si}}}{\dfrac{Wt_{W}}{At\ Wt_{W}} + \dfrac{Wt_{Mo}}{At\ Wt_{Mo}} + \dfrac{Wt_{Ti}}{At\ Wt_{Ti}} + \dfrac{Wt_{V}}{At\ Wt_{V}}}$$

Wt_{Si} = weight of silicon deposited in mg/cm^2.
Weight of each element = (w/o of element in suspension) (weight of modifier layer in mg/cm^2). For example, the weight of W in a Ti+V = 10 w/o suspension (64.3 w/o W + 25.7 w/o Mo + 5 w/o ti + 5 w/o V) was calculated as follows:

Wt_{W} = 0.643 (modifier weight gain).

3.3.2   Results

Results of the CVD runs made to determine deposition parameters are presented in Table VIII. This table lists the run number, characteristics of the specimen modifier layer (chemistry, weight gain and sintering temperature), CVD parameters (reactant gas mixture, reaction chamber pressure, reaction temperature and total deposition time), the resulting silicon content in the specimens in terms of both silicon weight gain and the atomic ratio of silicon to modifier layer. Initially, a series of deposition runs were made over the temperature range of 1800 to 2300°F (Runs 1 through 8). It was found that a non-adherent deposit was obtained below a reaction temperature of 2300°F. Light brushing removed the silicon and a small amount of the modifier layer as shown by the negative weight gains for Runs 1, 3 and 5. The remainder of the deposition runs were therefore made using a deposition temperature of 2300°F. Parameters that

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TABLE VIII

RESULTS OF CHEMICAL VAPOR DEPOSITION SILICIDING RUNS

Run No.	Spec. No.	Modifier Layer Total Ti+V Content (w/o)	Wt. Gain (mg/cm²)	Sintering Temp. (°F)	Nominal Thickness (mils)	CVD Parameters H₂ (Atm)	SiCl₄ (Atm)	H₂SiCl₄ Ratio	Reaction Chamber Pressure (Atm)	Reaction Temp. (°F)	Total Time (hrs)	Si Wt. Gain (mg/cm²)	Atomic Ratio Si/Mod.	Comments
1	A61	10	17.3	2760	2.0	0.40	0.10	4	0.10	1800	3	-1.0	-	Non-Adherent Coating
2	A62	10	25.6	2760	2.0	0.40	0.10	4	0.10	1800	-	-	-	Thermocouple Failure
3	A57	10	22.9	2760	2.0	0.40	0.10	4	0.10	1800	3	-4.1	-	Non-Adherent Coating
4	A16	10	26.0	2760	2.0	0.48	0.13	3.7	.185	2000	0.5	-	-	Manometer Failure
5	A58	10	40.1	2760	2.0	0.48	0.13	3.7	.185	2000	2	-0.5	-	Non-Adherent Coating
6	A18	10	50.1	2760	2.0	0.48	0.13	3.7	.185	2200	0.5	-	-	Solenoid Failure
7	A30	20	17.3	2940	2.0	1.27	.200	6.2	.185	2300	3	-	-	Specimen Contaminated
8	A'24	30	36.8	2940	2.0	1.40	.067	21	.185	2300	3	21.6	1.91	
9	A109	30	36.7	2760	3.5	1.4	.067	21	.167	2300	-	-	-	Thermocouple Failure
10	A38	30	51.4	2760	5.0	1.4	.067	21	.167	2300	-	-	-	Generator Failure
11	A127	10	26.6	2940	2.0	1.4	.067	21	.167	2300	4	11.0	1.80	
	A133	10	43.8		3.5							16.0	1.59	
	A144	10	54.0		5.0							19.6	1.58	
	A156	20	22.3		2.0							9.7	1.63	
	A164	20	44.5		3.5							14.9	1.24	
	A172	20	57.5		5.0							18.5	1.21	
	A178	30	19.0		2.0							8.3	1.21	
	A185	30	33.1		3.5							11.0	1.75	
	A193	30	49.6		5.0							7.4	1.09	Coating Delaminated

TABLE VIII (continued)

Run No.	Spec. No	Total Ta-V Content (w/o)	Wt. Gain (mg/cm²)	Sintering Temp. (°F)	Nominal Thickness (mils)	H₂ (Atm)	SiCl₄ (Atm)	H₂:SiCl₄ Ratio	Reaction Chamber Pressure (Atm)	Reaction Temp. (°F)	Total Time (hrs)	Si Wt. Gain (mg/cm²)	Atomic Ratio Si/Mod.	Comments
12	A128	-	-	-	-	1.4	.067	21	.167	2300	-	-	-	Solenoid Failure
13	A136	10	31.7	2940	2.0	1.4	.067	21	.167	2300	7.5	13.1	1.79	
	A148	10	45.3		3.5							18.4	1.77	
	A158	10	52.3		5.0							20.3	1.69	
	A166	20	22.9		2.0							10.0	1.63	
	A173	20	44.0		3.5							17.0	1.44	
	A179	20	57.5		5.0							20.7	1.35	
	A188	30	17.1		2.0							7.3	1.40	
	A195	30	33.3		3.5							12.0	1.18	
		30	49.9		5.0							16.5	1.08	
14	A131	10	26.8	2940	2.0	0.735	.067	11	.167	2300	5.5	2.9	2.06	Exit Valve Sticking, Cold Trap Plugging
	A137	10	47.7		3.5							20.5	1.86	
	A149	10	50.8		5.0							21.9	1.87	
	A163	20	23.5		2.0							11.8	1.86	
	A167	20	44.2		3.5							18.6	1.57(a)	
	A175	20	56.5		5.0							23.8	2.54(a)	
	A181	30	17.2		2.0							18.7	1.60	
	A189	30	31.9		3.5							13.6	1.39	
	A198	30	47.3		5.0							17.1	1.17	
15	A132	10	26.8	2940	2.0	0.769	.134	5.74	.167	2300	5.0	13.6	2.20	Exit Valve Sticking, Cold Trap Plugging
	A143	10	45.5		3.5							20.1	1.90	
	A152	10	49.7		3.5+							22.1	1.93	
	A161	20	26.9		2.0							13.4	1.86	
	A171	20	44.5		3.5							19.0	1.59	
	A176	20	57.4		5.0							24.0	1.56	
	A200	30	17.9		2.0							9.7	1.77	
	A183	30	18.7		2.0							9.9	1.73	
	A190	30	31.9		3.5							13.7	1.43	

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TABLE VIII (continued)

Run No.	Spec. No.	Total T+V Content (w/o)	Modifier Layer Wt. Gain (mg/cm²)	Sintering Temp. (°F)	Nominal Thickness (mils)	CVD Parameters H₂ (Atm)	SiCl₄ (Atm)	H₂SiCl₄ Ratio	Reaction Chamber Pressure (Atm)	Reaction Temp. (°F)	Total Time (hrs)	Si Wt. Gain (mg/cm²)	Atomic Ratio Si/Mod.	Comments
16	A199	10	26.2	2940	2.0	.800	.067	11.9	.200	2300	4.0(b)	11.9	1.97	Exit Valve
	A139	10	44.3		3.5							17.0	1.66	Sticking, ...
	A147	10	50.3		5.0							18.8	1.62	Trap Plugging
	A157	20	25.2		3.5+							11.3	1.68	
	A163	20	46.1		5.0							15.7	1.27	
	A187	20	58.1		2.0							20.5	1.32	
	A201	30	18.7		3.5							7.3	1.27	
	A206	30	34.5		5.0							10.1	0.96	
	A213	30	52.1									14.9	0.94	
17	A130	10	24.5	2760	2.0	1.4	.067	21	0.4	2300	5.0	11.8	2.09	
	A140	10	43.0		3.5							18.6	1.78	
	A150	10	51.9		5.0							13.1	1.10	
	A162	20	22.7		2.0							11.4	1.88	
	A170	20	45.3		3.5							17.5	1.45	
	A186	20	61.2		5.0							22.9	1.40	
	A202	30	18.8		2.0							7.3	1.28	
	A207	30	48.1		3.5							12.2	0.83	Coating Partially Delaminated
	A212	30	53.2		5.0							-		Coating Completely Delaminated
18	A135	10	22.7	2760	2.0	1.4	.067	21	0.4	2300	10	16.1	3.08	
	A146	10	39.4		2.5							22.6	2.48	
	A151	10	41.4		3.5							22.6	2.38	
	A168	20	20.3		2.0							14.3	2.62	
	A182	20	40.3		3.5							21.2	1.97	
	A194	20	53.9		5.0							25.7	1.78	Edge Delamination
	A205	30	18.8		2.0							13.8	2.28	
	A209	30	34.4		3.5							17.3	1.64	Edge Delamination
	A216	30	50.9		5.0							-	-	Complete Delamination

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TABLE VIII (continued)

Run No.	Spec. No.	Modifier Layer — Total Ti+V Content (w/o)	Wt. Gain (mg/cm²)	Sintering Temp. (°F)	Nominal Thickness (mils)	CVD Parameters — H₂ (Atm)	SiCl₄ (Atm)	H₂:SiCl₄ Ratio	Reaction Chamber Pressure (Atm)	Reaction Temp. (°F)	Total Time (hrs)	Si Wt. Gain (mg/cm²)	Atomic Ratio Si/Mod.	Comments
19	-	-	-	-	-	-	-	-	-	-	-	-	-	Equipment Failure
20	A134	10	20.3	2760	2.0	1.4	.067	21	0.4	2300	7.5	11.8	2.53	
	A153	10	44.9		3.5							22.3	2.16	
	A165	20	23.2		2.0							13.5	2.17	Complete Delamination
	A192	20	54.9		5.0								-	
	A204	30	18.7		2.0							11.8	2.06	
	A211	30	33.5		3.5							15.3	0.994	Corners Delaminated
	A215	30	49.5		5.0								-	Complete Delamination
21	A291	10	59.5	2760	5.0				0.6			1.8	-	White Powder on Specimens and Reaction Chamber.
	A297	10	56.3		5.0							2.2	-	
	A315	30	21.8		2.0							2.7	-	
	A352	30	57.2		5.0							7.8	-	
	A353	30	55.7		5.0							6.7	-	
22	A97	10	56.8	2940	5.0						5.5	-	-	White Powder on Specimens and Reaction Chamber
	A98	10	54.9		5.0							-	-	
	A129	30	21.4		2.0							-	-	
	A156	30	52.2		5.0							-	-	
	A157	30	53.5		5.0							-	-	
23	-	-	-	-	-						0.5	-	-	Reaction Chamber Exit Valve Malfunction
24	A306	10	56.3	2940	5.0						4.5	24.1	1.51	
	A328	30	20.5		2.0							10.8	1.72	
	A354	30	55.4		5.0							19.2	1.13	

NOTES (a) Surface cracks on specimen, substrate exposed to Si.
       (b) Reaction time = 36 seconds per cycle.

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were varied in these runs included the ratio of H_2 to $SiCl_4$, reaction chamber pressure, cyclic reaction time and total deposition time. The effects of these parameter variations on the atomic ratio of silicon to modifier elements are summarized in Figures 22 through 27.

Figure 22 shows the silicon/modifier layer atomic ratio as a function of the $H_2/SiCl_4$ ratio at a reaction chamber pressure of 0.167 Atm. Deposits were made on modifier layers of all three chemistry variations and all three thickness levels using $H_2/SiCl_4$ ratios of 5.74, 11.0 and 21.0. A range of silicon/modifier atomic ratios was obtained over the various thickness levels for each chemistry variation as indicated by the bar graphs. The data shows that decreasing the $H_2/SiCl_4$ ratio increased the amount of silicon deposited. For example, with a $H_2/SiCl_4$ ratio of 5.74, the silicon/modifier atomic ratio ranged from 1.08 to 1.79 after a deposition time of 7.5 hours. The lower $H_2/SiCl_4$ ratios (5.74 and 11.0), however, resulted in larger amounts of unreacted $SiCl_4$. Condensation of the $SiCl_4$ resulted in frequent sticking of the solenoid at the reaction chamber exhaust and plugging of the cold trap. When the malfunctions occurred, the cycle was interrupted (reaction chamber blocked off under vacuum) and the cold trap exit solenoid was cleaned. (The deposition times do not include the downtime for component cleaning.) In order to decrease the amount of unreacted $SiCl_4$, an additional run (No. 16 in Table VII) was made using a longer cyclic reaction time (36 seconds instead of 16 seconds). The $H_2/SiCl_4$ ratio for this run was 11.9 and the reaction chamber pressure was increased slightly (from 0.167 to 0.200 atm). Increasing the cyclic reaction time did not eliminate solenoid sticking and plugging of the cold trap. All further deposition runs were then made using a $H_2/SiCl_4$ ratio of 21.

As indicated in Figure 22, under constant deposition conditions, the silicon to modifier layer atomic ratio varied with modifier layer composition and thickness. Figure 23 illustrates the extent of this variation for Run No. 13 but was typical for all of the runs This figure is a plot of the silicon/modifier atomic ratio as a function of modifier layer weight gain for the three suspension compositional variations. For a given modifier layer composition, silicon to modifier atomic ratio decreased with increasing modifier layer thickness (as reflected by modifier layer weight gain). For example, specimens with modifier

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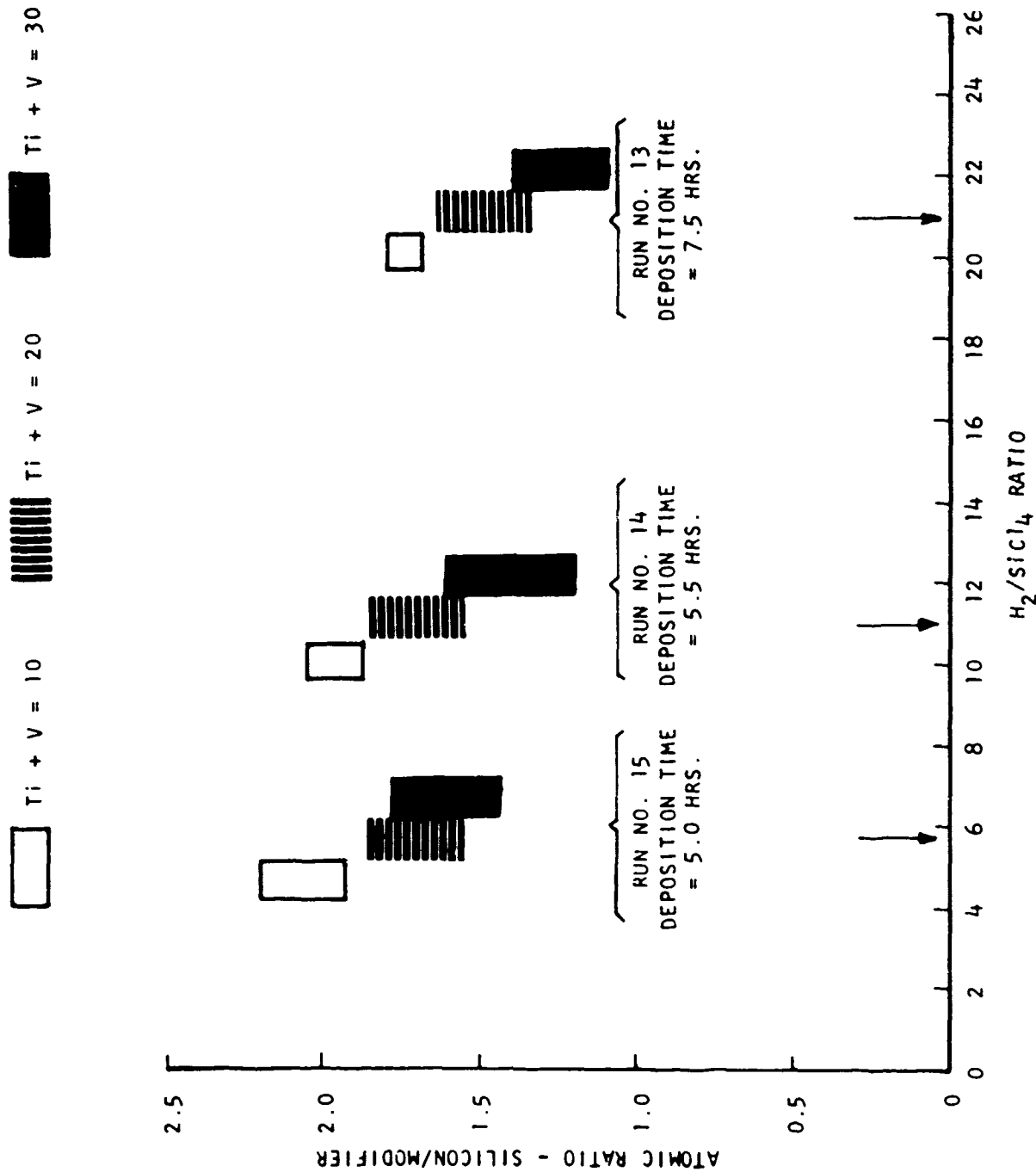
Figure 22. Effect of $H_2/SiCl_4$ Ratio on Silicon/Modifier Atomic Ratio at a Reaction Chamber Pressure of 0.167 Atm.
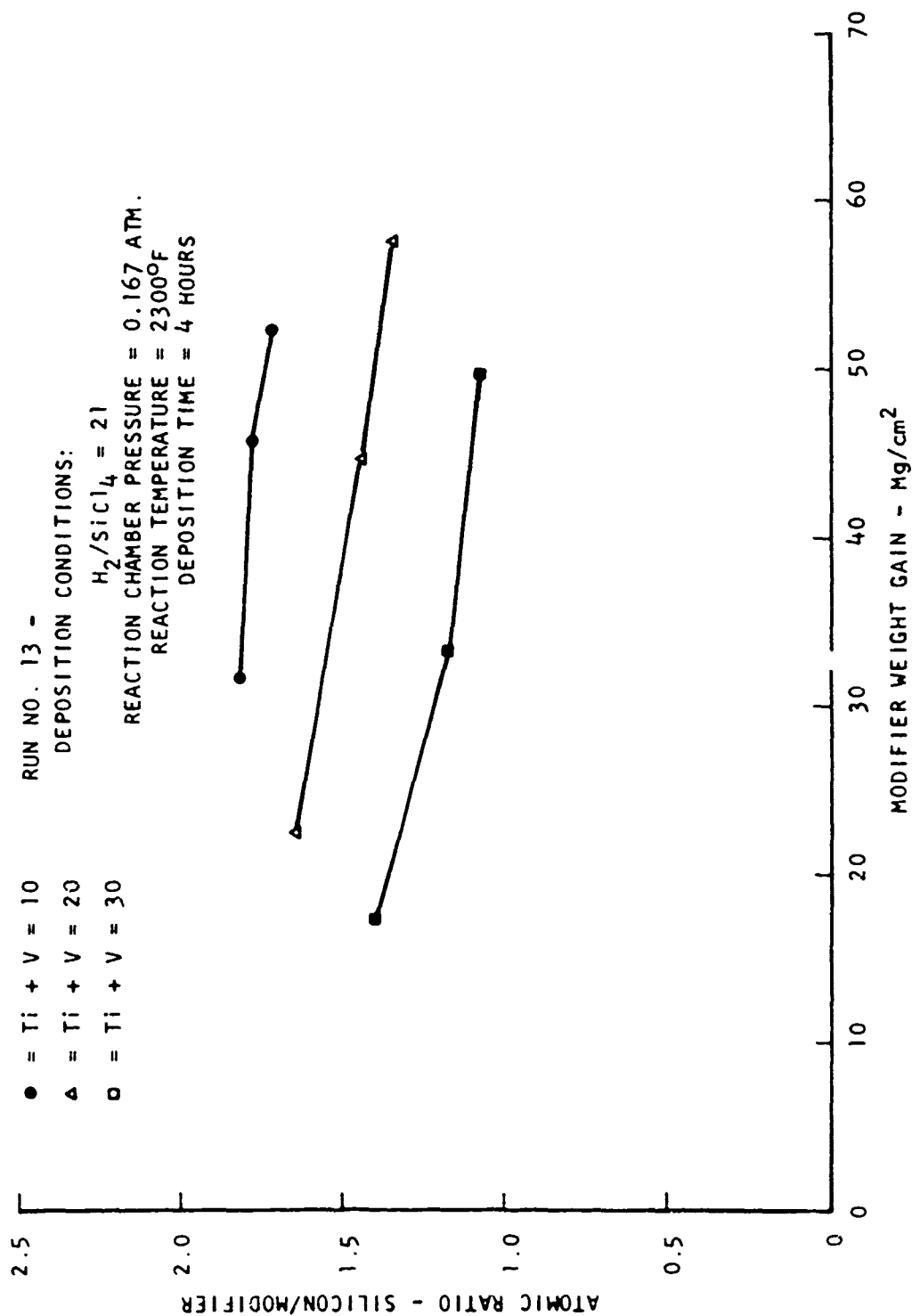
Figure 23. Effect of Modifier Layer Composition and Thickness on Silicon/Modifier Atomic Ratio at Constant Deposition Conditions.

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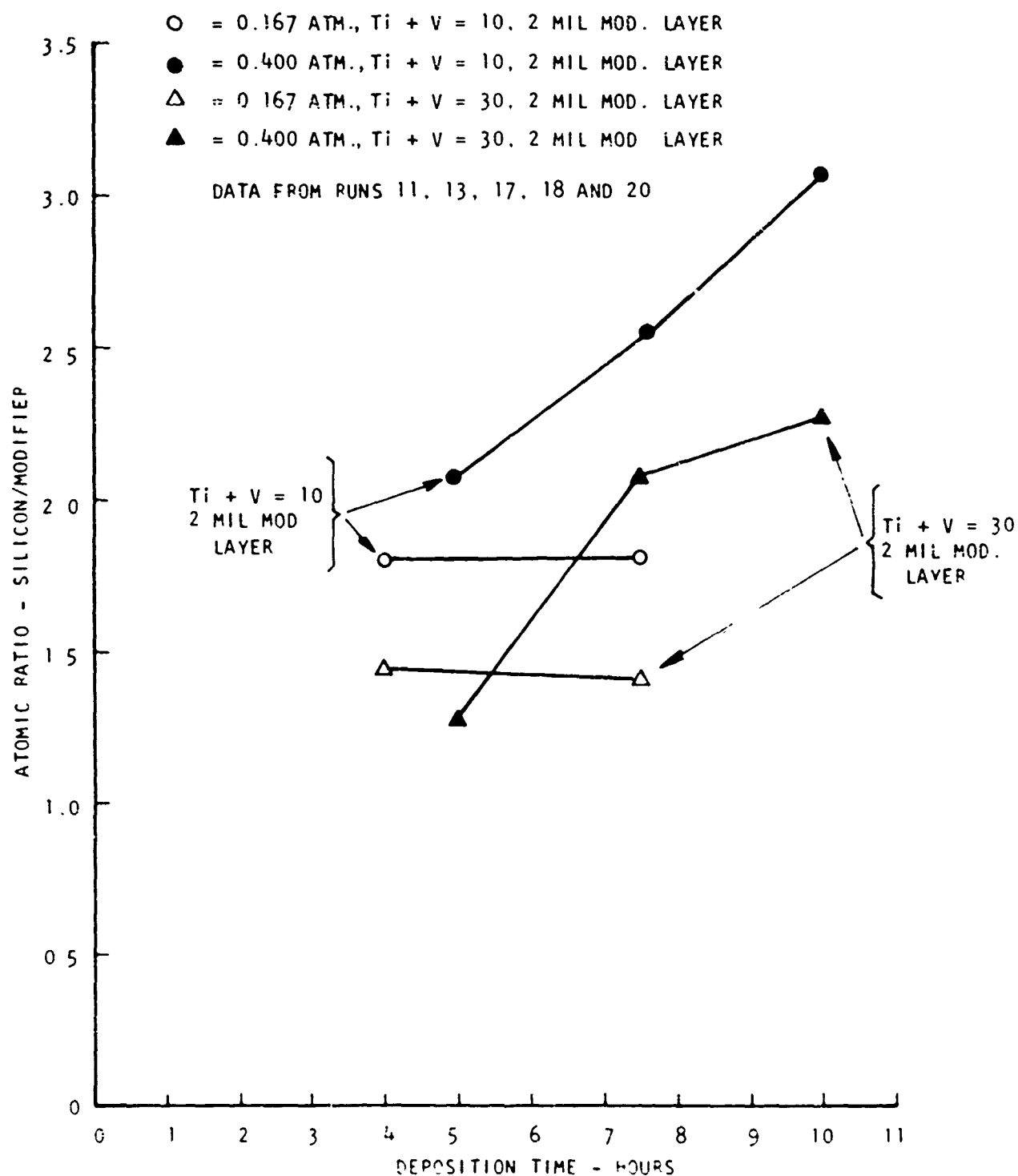
Figure 24. Effect of Reaction Chamber Pressure on Silicon/Modifier Atomic Ratio of 2 Mil Thick Modifier Layers.
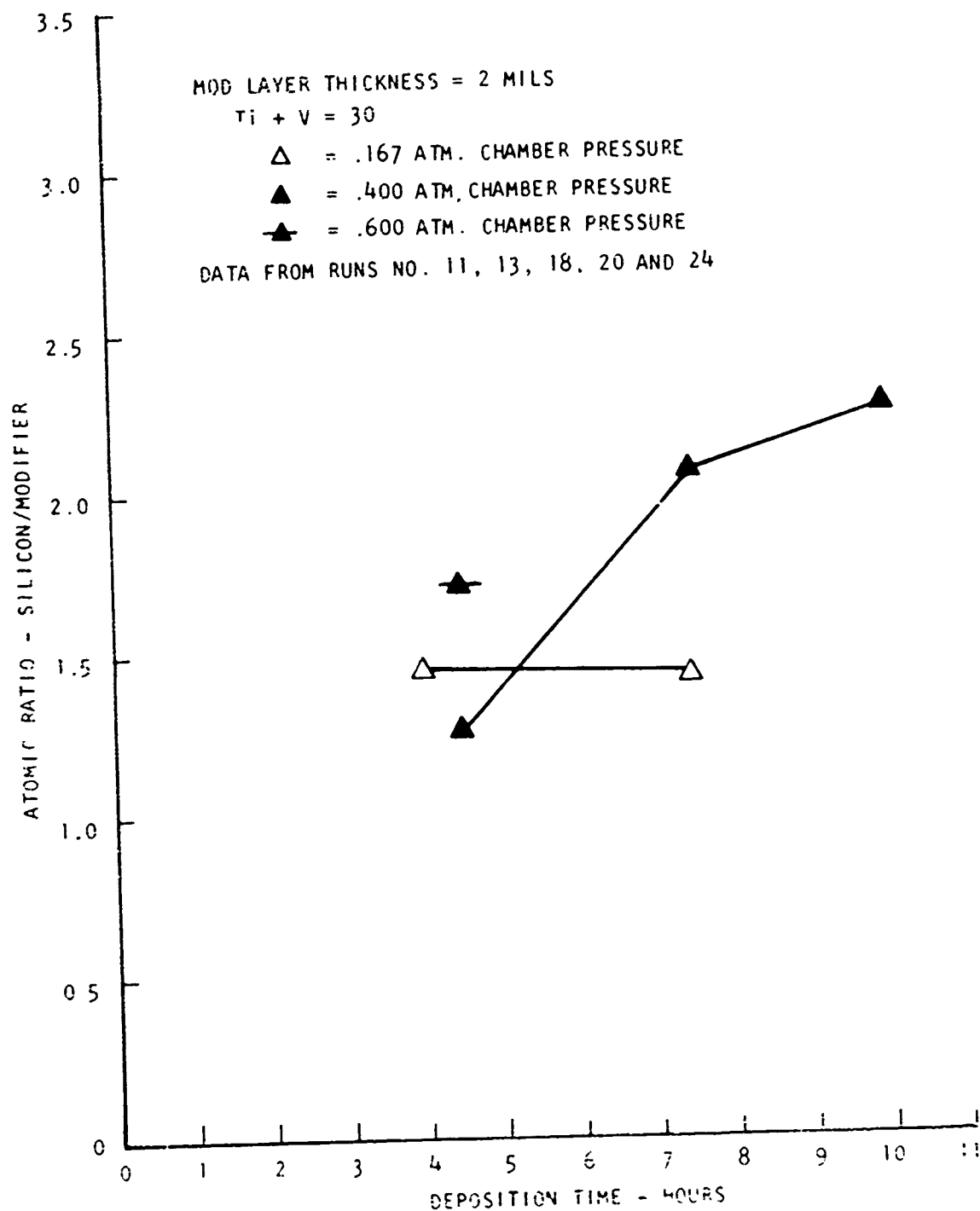
Figure 25. Effect of Reaction Chamber Pressure on Silicon Modifier Atomic Ratio of 2 Mil Thick Modifier Layers.

Figure 26. Effect of Reaction Chamber Pressure on Silicon/Modifier Atomic Ratio of 5 Mil Thick Modifier Layers.
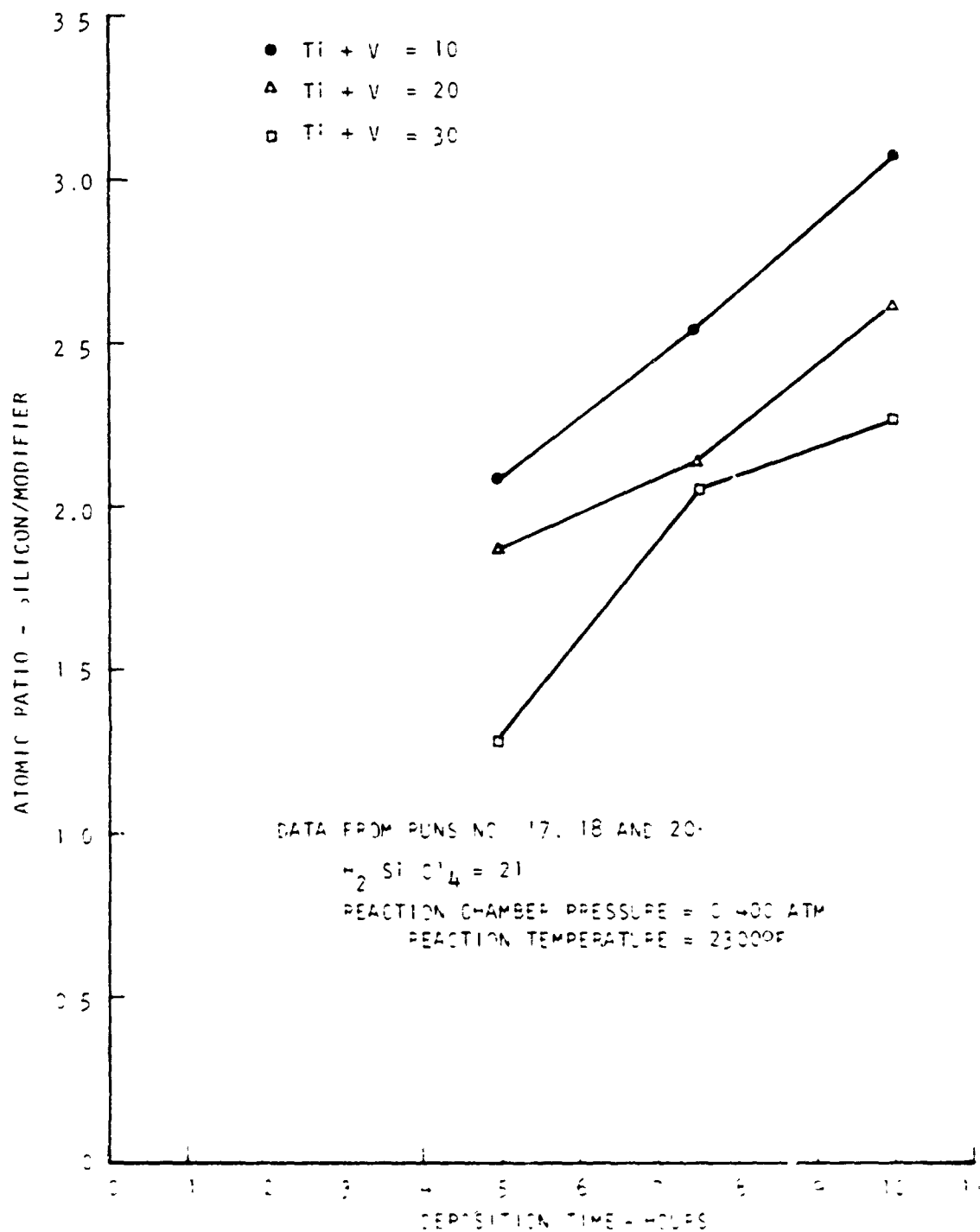
Figure 27. Effect of Deposition Time on Silicon Modifier Atomic Ratio for 2 Mil Thick Modifier Layers.

layers deposited from suspensions containing Ti+V contents of 10 w/o had
atomic/modifier ratios of 1.79, 1.77 and 1.69 for nominal modifier layer thick-
nesses of 2.0, 3.5 and 5.0 mils, respectively. At a given modifier layer thick-
ness level, the silicon/modifier atomic ratio decreased with increasing Ti+V
content of the modifier layer. For example, specimens with nominal 2.0 mil thick
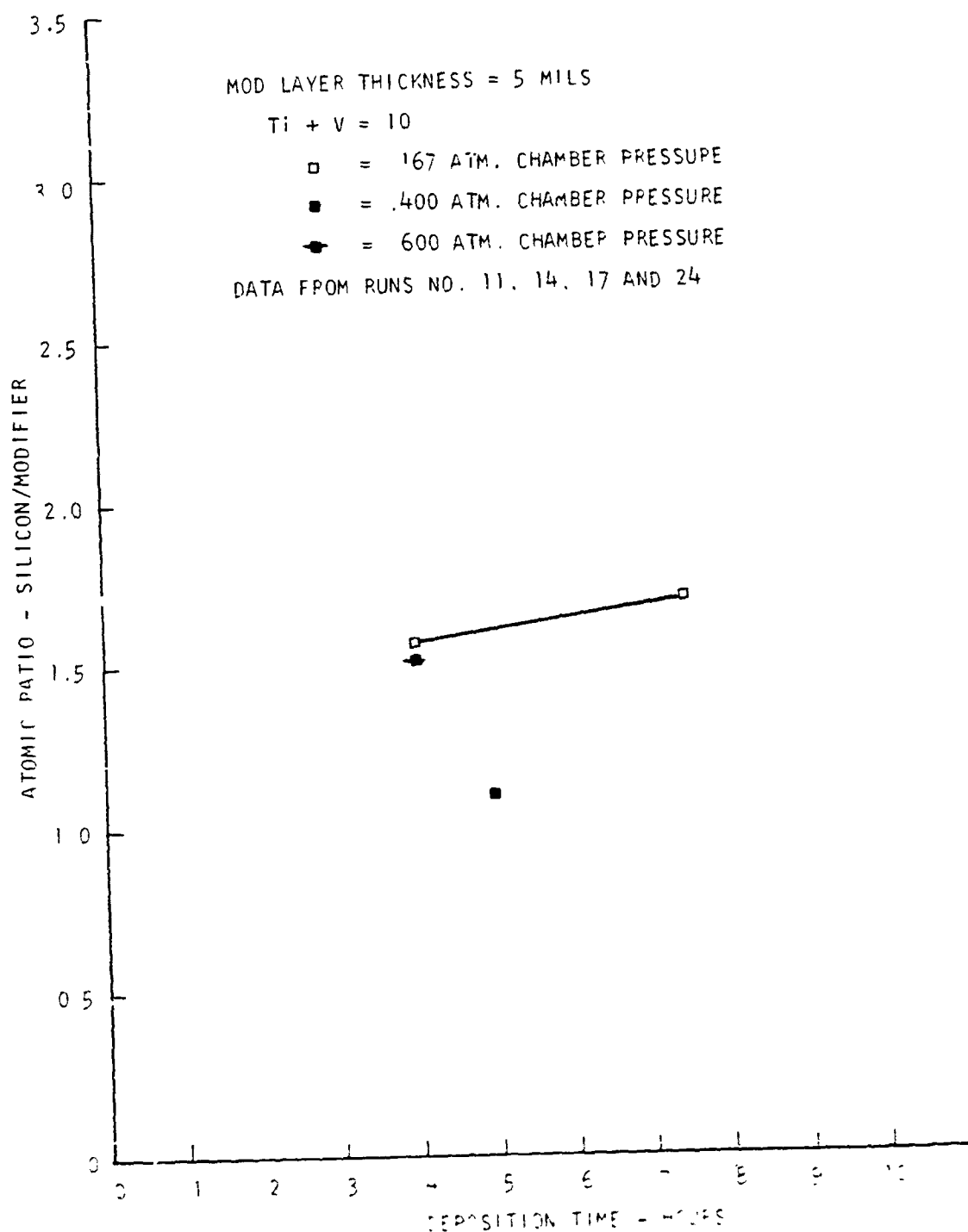modifier layers that were deposited from suspension containing Ti+V contents of
10, 20 and 30 w/o had silicon to modifier atomic ratios of 1.79, 1.63 and 1.40,
respectively.

For the majority of the deposition trials, reaction chamber pressure was
either 0.167 atm or 0.400 atm. A small amount of data was obtained from one
additional run in which the reaction chamber pressure was 0.600 atm. In general,
increasing the reaction chamber pressure from 0.167 atm to 0.400 atm increased
the silicon to modifier layer atomic ratio for a given modifier layer thickness
and composition as illustrated in Figure 24. Figure 24 shows the silicon to
modifier layer atomic ratios obtained for nominal 2 mil thick modifier layers as
a function of deposition time at reaction chamber pressures of 0.167 and 0.400
atm. In general, for a given deposition time, the higher reaction chamber pressure
produced a higher silicon to modifier layer atomic ratio. For example, after a
7.5 hour deposition time, deposits made from suspensions containing a Ti+V
content of 10 w/o had silicon to modifier atomic ratios of 1.79 and 2.53 for
reaction chamber pressures of 0.167 and 0.400 atm, respectively. Increasing the
reaction chamber pressure to 0.600 atm increased the silicon to modifier layer
atomic ratio for 2 mil thick specimens deposited from suspensions containing a
Ti+V content of 10 w/o as shown in Figure 25 but had no effect on 5 mil thick
specimens deposited from the same suspension composition as shown in Figure 26.

The effect of deposition time was determined for reaction chamber pressures
of 0.167 and 0.400 atm. Within the experimental conditions investigated, the
effect of deposition time appeared to be different for the two reaction chamber
pressures. With a reaction chamber pressure of 0.167 atm (runs 11 and 13)
increasing the deposition time from 4 hours to 7.5 hours appeared to increase the
silicon to modifier atomic ratios to a limiting value. The limiting value was
dependent on modifier layer composition. The silicon to modifier atomic ratios
for specimens with 2.0 and 3.5 mil thick modifier layers deposited from 10 w/o

Ti+V suspensions were 1.79 and 1.77 at a deposition time of 7.5 hours. These values were approximately the same as those obtained with a deposition time of 4 hours. Approximately the same silicon to modifier atomic ratios were obtained for 2.0 mil thick modifier layers deposited from suspensions containing Ti+V contents of 20 w/o or 30 w/o at deposition times of 4 hours and 7.5 hours. All of the other modifier layer thickness/composition combinations had increased silicon to modifier atomic ratios with increasing deposition time, but these values were not as great as the above values. Thinner modifier layers with lower Ti+V contents appeared to reach the limiting atomic ratio in less time. At a reaction chamber pressure of 0.400 atm, increasing the deposition time increased the silicon to modifier atomic ratio for all modifier layer/thickness combinations. This is illustrated in Figure 27 for 2 mil thick modifier layers deposited from suspensions containing Ti+V contents of 10, 20 and 30 w/o.

The influence of specimen and deposition parameter variations on the silicon/modifier layer atomic ratio is summarized below:

1. Effect of Modifier Layer Variations -
   At constant deposition conditions, decreasing the modifier layer thickness and Ti+V content increased the silicon to modifier layer atomic ratio.

2. Effect of $H_2/SiCl_4$ Ratio -
   Decreasing the $H_2/SiCl_4$ ratio increased the silicon to modifier layer atomic ratio.

3. Effect of Reaction Chamber Pressure -
   Increasing the reaction chamber pressure to 0.400 atm increased the silicon to modifier layer atomic ratio.

4. Effect of Deposition Time -
   At a reaction chamber pressure of 0.167 atm, increasing the deposition time increased the silicon to modifier atomic ratio to a limiting value. However, at a reaction chamber pressure of 0.400 atm, increasing the deposition time increased the silicon to modifier atomic ratio for all of the deposition times investigated.

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Data obtained from the parameter development work indicated that silicon to modifier atomic ratios could be produced for seven of the combinations required for the factorial experiment. The required ratios could be produced by using a $H_2/SiCl_4$ ratio of 21, a reaction chamber pressure of 0.400 atm, a deposition temperature of $2300^\circ F$ and adjusting the deposition time for a particular modifier layer/thickness combination. The following table summarizes these combinations and the deposition times required to produce the required silicon to modifier atomic ratios.

Modifier Layer		Si/Modifier	Deposition
Ti+V w/o	Thickness (mils)	Atomic Ratio	Time (hrs)
10	2.0	2.1	5.0
10	2.0	2.5	7.5
10	2.0	3.0	10.0
10	3.5	2.1	7.5
20	2.0	2.1	7.5
20	2.0	2.5	10.0
30	2.0	2.1	7.5

Extrapolation of the data indicated that deposition times on the order of 15-20 hours would be required to obtain the required silicon to modifier atomic ratios for the heavier modifier layers. These deposition times were not considered practical with the present deposition equipment for the reasons to be described below. Nor was modification of the equipment possible within the program funding and schedule. Throughout the chemical vapor deposition development work, con- siderable difficulties were experienced in operating the equipment. The high temperature, lengthy deposition time, $SiCl_4$ and HCl (reaction product) produced a severely corrosive environment in which commercially available components frequently failed. This resulted in aborted deposition runs and frequent replace- ment and maintenance of the components in the system. The components included vacuum regulators, solenoid valves, pressure gages, O-ring seals and refractory insulators. They required cleaning or replacement of critical parts after lengthy deposition runs. Vacuum regulators, solenoid valves and pressure gages required cleaning after each run to remove condensed $SiCl_4$. They would have to perform at a temperature of at least $150^\circ F$ to prevent condensation of the $SiCl_4$ The O-rings on these components as well as those on the reaction chamber were subject to corrosive attack and loss of elasticity. Of the various O-ring compounds tried, fluorocarbon elastomers provided the most satisfactory performance. All of

the solenoid valve seats, particularly the valve on the reaction chamber, were subject to corrosion from $SiCl_4$ or a combination of $SiCl_4$ and HCl. Diaphragms on the vacuum regulators were subject to loss of elasticity and cracking.

In view of the above equipment difficulites and the projected deposition times necessary for obtaining the required silicon to modifier atomic ratios for the heavier modifier layers, CVD parameter development was discontinued. Silicon was deposited on a number of specimens using the parameters developed above, and the specimens were oxidation tested. This work is described in the next section.

3.4 Oxidation Tests

3.4.1 Procedure

Additional chemical vapor deposition runs were made to provide coupon and bend test specimens for oxidation testing. Two of the variable combinations that were to be used in the fractional factorial experiment were used for the coupons and bend test specimens. These combinations were:

Combination 1 -

    Modifier Layer Thickness - 2.0 mils

    Ti+V - 10 w/o

    Sintering Temperature - $2760^{\circ}F$

    Silicon/Modifier Atomic Ratio - >2.1

Combination 6 -

    Modifier Layer Thickness - 2.0 mils

    Ti+V - 30 w/o

    Sintering Temperature - $2940^{\circ}F$

    Silicon/Modifier Atomic Ratio - ·2.1

Combination 1 was used for both 20 and 40 mil thick substrates, while combination 6 was used only on 20 mil thick substrates. Selected coupons from both combinations were oxidation exposed in static air at $2500^{\circ}F$. After 20 hours of exposure, the specimens were removed from the furnace and examined.

3.4.2 Results

Results of the chemical vapor deposition runs made for the variable combinations are presented in Table IX. Variations in silicon to modifier atomic ratio

TABLE IX

RESULTS OF CHEMICAL VAPOR DEPOSITION RUNS MADE FOR OXIDATION TESTS

Combination No.(a)	Substrate Thickness (mils)	Specimen Type(b)	Specimen No.	Modifier Layer (mg/cm²)	CVD Run(s)	Total Deposition Time (hrs)	Atomic Ratio Si/Mod.
1	20	C	257	28.7	25+27	7	2.37
			258	26.9			2.52
			259	27.5			2.52
			260	28.0			2.48
			261	27.2	↓		2.81
			265	25.1	25		2.13
			266	26.6	25		2.27
		B.T.	7	25.7	25+27		2.88
1	40	C	41	28.0	28	6	2.40
			42	27.1			2.15
			43	27.7			2.16
			44	28.9			2.22
			45	27.7			2.33
			56	27.7			2.42
			57	29.8			2.37
		B.T.	2	19.8			2.71
			3	26.9			2.11
			4	24.7			2.84
			5	25.0			3.50
6	20	C	323	22.3	26+27	7	2.08
			324	19.4			2.23
			325	19.2			2.46
			326	18.6	↓	↓	2.31
			327	19.4	26	5	1.13
			329	18.7			0.18
			330	19.3			0.66
		B.T.	41	24.5			0.35
			42	19.5			1.49
			43	21.0			1.52
			44	21.9			1.52

NOTES: (a) Combination No. 1 – Ti + V = 10 w/o, Modifier Thickness = 2.0 mils
Sinter Temperature = 2760°F
Si/Modifier Atomic Ratio = ·2.1

Combination No. 6 – Ti + V = 30 w/o, Modifier Thickness = 2.0 mils
Sinter Temperature = 2940°F
Si/Modifier Atomic Ratio = 2.1

(b) Specimen Type – C – coupon
BT – bend test specimen

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were obtained in specimens processed inthe same run. This variation is attributed
to variations in modifier layer thickness and rack position in the reaction
chamber. As discussed previously, for constant deposition conditions, a higher
silicon to modifier atomic ratio was obtained for thinner modifier layers. For
these runs, the number of specimens required that all rack positions be utilized.
Specimens at the bottom of the reaction chamber had higher silicon to modifier
atomic ratios (for equivalent modifier layer thickresses). This increase was
probably due to impingement of the reactant gases as the chamber was filled for
each reaction cycle. To alleviate this problem, an improved baffling system
would have to be installed at the bottom of the chamber to prevent impingement
of the reactant gases on the lower rack positions.

Runs 25 and 26 indicated that the deposition times determined in the
parameter development work would have to be extended to obtain the desired
Si/modifier atomic ratios. For example, in the parameter development work, five
hours would produce a Si/modifier atomic ratio of >2.1 for combination No. 1.
In run No. 25, a five-hour deposition time produced this ratio in only two
specimens (coupons 265 and 266) and the ratio was marginal in these specimens
(2.13 and 2.27). As a result selected specimens from runs 25 and 26 were
processed for an additional two hours in run No. 27. The additional deposition
time required was probably due to the larger specimen surface area in the
reaction chamber for these runs as compared to the parameter development runs.

The appearance of the coupons after oxidation exposure at $2500^{o}F$ is
shown in Figures 28 and 29. All of the specimens had failed during the 20 hour
exposure. In instances where the specimens did not fail catastrophically, the
criterion for failure was oxidation penetration into the substrate. Oxidation
penetration nto the substrate was determined by the appearance of the substrate
oxidation product (beige in color). Two of the coupons failed catastrophically
(Figure 28a) and the failure initiation sites could not be determined. Appearance
of the remainder of the coupons indicated that failures were initiated at corners
or edges. Areas of the corners that were gripped by the electrodes during
electrophoretic deposition and subsequently manually patched did not fail.
Figure 30 shows the coating microstructure at the edges of specimen No. 42
(Figure 28b). One corner of the specimen had failed catastrophically. The

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#265
S/m = 2.13

#266
S/m = 2.27

#257
S/m = 2.37

#42
S/m = 2.15

#44
S/m = 2.16

(a) Substrate Thickness - 20 mils
Ti + V = 10 w/o
Modifier Layer Thickness - 2.0 mils
Sintering Temperature - 2760°F
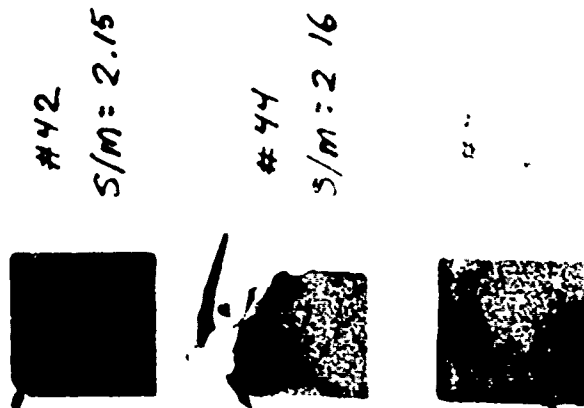
(b) Substrate Thickness - 40 mils
Ti + V = 10 w/o
Modifier Layer Thickness - 2.0 mils
Sintering Temperature - 2760°F

Figure 28.   Appearance of Coated Coupons After 20 Hours Oxidation
Exposure at 2500°F (Combination No. 1)   (1X)

#323
S/m: 2.08

#324
S/m: 2.23

Substrate Thickness - 20 mils
Ti + V = 30 w/o
Sintering Temperature - 2940°F

Figure 29. Appearance of Coated Coupon After 20 Hours Oxidation
Exposure at 2500°F (Combination No. 6)   (1X)

(a)

(b)

Figure 30. Coating Microstructure of Specimen No. 42 at Specimen Edges After Oxidation Exposure of 20 Hours at 2500°F
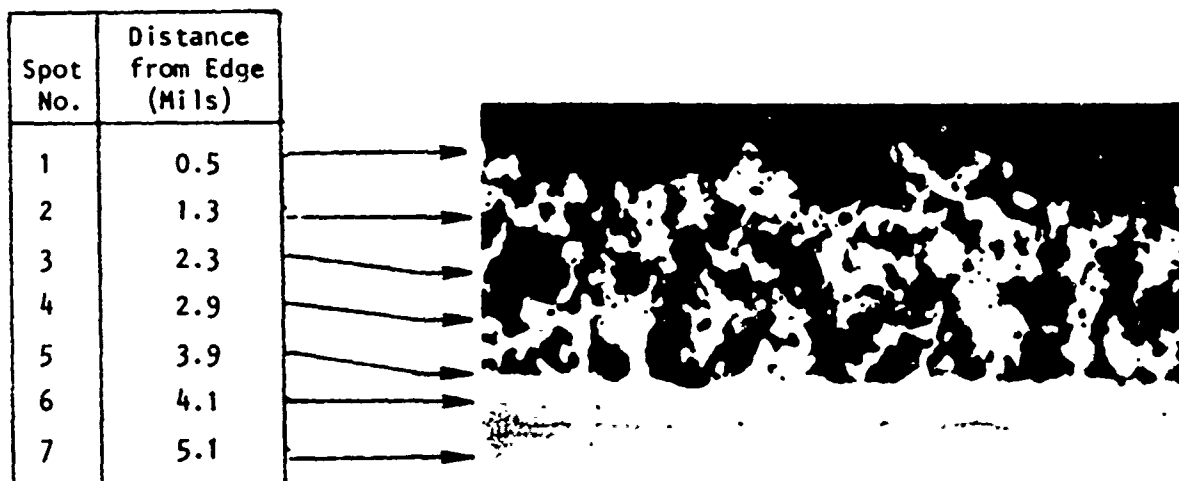
Etch - 15 v/o Lactic Acid + 5 v/o HCl + 5 v/o HNO_3 + 75 v/o H_2O
Magnification - 400X

specimen was sectioned away from the corner that failed catastrophically. As shown in Figure 30, oxidation has penetrated through the outer coating and diffusion zone at the edges. In Figure 30a, the oxidized coating and diffusion zone have separated from the specimen. Oxidation products cover the outer surface of the coating adjacent to the edges but have not penetrated through the outer coating. This anomalous oxidation behavior of edges and corners has been reported for another silicide coating (Cr-Si-Ti) deposited by pack cementation on columbium alloys[21]. The reason for this anomalous behavior could not be determined. Edge and corner failures were not a function of substrate radius, coating thickness or chemical composition of the coating (ratio of Si to Cr+Ti).

After oxidation testing, one exposed specimen from each combination of variables was selected for electron microprobe analysis along with comparable specimens in the as-deposited condition. The analyses were performed on a Philips AMR/3 electron microprobe analyzer. Elements in the substrate and additional pure elements (Ti, V, Mo and Si) were used as standards. Weight and atomic percentages of the elements were determined by Colby's Magic IV computer program. Spot analyses were made in the outer coating, the diffusion zone and the substrate adjacent to the diffusion zone. The atomic ratio of silicon-to-modifier elements was calculated from the microprobe data where appropriate.

Results of microprobe analyses made on the sides of the specimens are shown in Figures 31 through 34. Figures 31 and 32 show the results obtained on specimens with modifier layers deposited from suspensions containing Ti+V contents of 10 w/o in the as-deposited condition and after exposure at 2500°F. Figures 33 and 34 show the results obtained on specimens with modifier layers deposited from suspensions containing Ti+V contents of 30 w/o. No trends in composition could be distinguished for either the as-deposited condition compared to the exposed condition or for coatings with a modifier layer deposited from a suspension with a Ti+V content of 10 w/o compared to a coating with a modifier layer deposited from a suspension with a Ti+V content of 30 w/o.

In all instances, Ti and V levels were the lowest in the outer coating. The levels of these elements in this area ranged from 0.02 w/o to 3.72 w/o with the majority of the areas having less than 1 0 w/o. The outer portion of the

Spot No.	Distance from Edge (Mils)
1	0.5
2	1.3
3	2.3
4	2.9
5	3.9
6	4.1
7	5.1

Etch - 15 v/o Lactic Acid + 5 v/o HCl + 5 v/o HNO_2 + 75 v/o H_2O

Magnification 400X

Spot No.	Composition (wt %)								Silicon to Modifier At. Ratio
	Mo	V	Ti	Si	Nb	Zr	Ta	W	
1	0	0.67	0.26	41.22	-	-	-	65.89	3.89
2	0	0.69	0.22	35.57	-		-	63.32	3.49
3	6.73	0.73	1.93	42.60	-	-	-	61.03	3.32
4	5.45	0.70	1.02	43.76	0.20	0.03	0.02	65.64	3.47
5	1.60	1.93	3.59	24.60	38.58	0.30	21.20	8.97	-
6	0.05	0.02	0.06	37.74	35.81	0.03	9.56	6.15	-
7	0.16	0	0.01	0.05	60.01	0.27	28.65	10.53	-

Figure 31. Electron Microprobe Analysis of Specimen No. 45.
Coating Condition - As-Deposited
Nominal Modifier Layer Thickness - 2 mils
Suspension Ti+V Content - 10 w/o
Sintering Temperature - 2760°F

Spot No.	Distance from Edge (Mils)
1	0.3
2	1.4
3	2.7
4	3.5
5	4.4
6&7	4.9
8	5.7

Etch - 15 v/o Lactic Acid + 5 v/o HCl + 5 v/o HNO_3 + 75 v/o H_2O

Magnification 400X

Spot No.	Composition (wt %)								Silicon to Modifier At. Ratio
	Mo	V	Ti	Si	Nb	Zr	Ta	W	
1	52.79	0.02	0.06	38.45	-	-	-	0.25	2.47
2	39.29	0.02	0.05	39.51	-	-	-	15.86	2.83
3	11.91	0.02	0.05	30.17	-	-	-	54.43	2.55
4	46.63	0.02	0.05	35.34	0.05	0.03	0.07	16.02	2.19
5	3.56	1.01	2.33	26.01	48.27	0.21	21.75	12.11	-
6	0.30	0.17	1.20	26.23	62.37	0.35	25.53	10.07	-
7	0.25	0.08	0.66	25.15	58.58	0.28	25.51	9.48	-
8	0.04	0.02	0.05	0.01	65.62	0.83	28.81	9.84	-

Figure 32. Electron Microprobe Analysis of Specimen No. 42.
Coating Condition - Oxidation Exposed, 20 Hrs at 2500°F
Nominal Modifier Layer Thickness - 2 Mils
Suspension Ti+V Content - 10 w/o
Sintering Temperature - 2760°F

Spot No.	Distance from Edge (Mils)
1	0.6
2	1.2
3	2.8
4	3.6
5&6	3.9
7	4.9

Etch - 15 v/o Lactic Acid + 5 v/o HCl + 5 v/o
HNO$_3$ + 75 v/o H$_2$O

Magnification - 400X

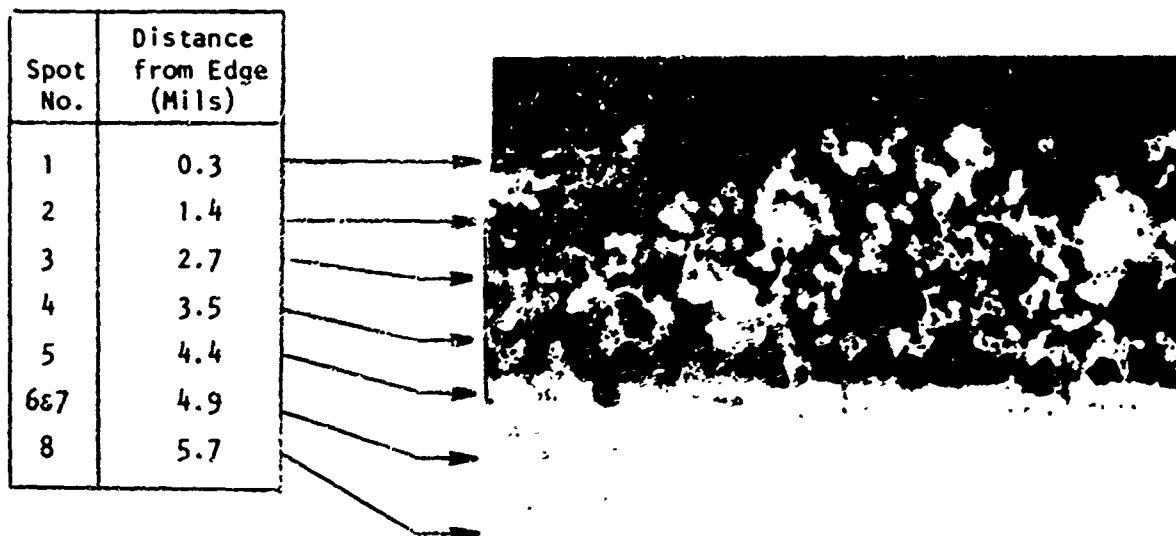| Spot No.	Composition (wt %)								Silicon to Modifier At. Ratio
	Mo	V	Ti	Si	Nb	Zr	Ta	W	
1	1.11	0.56	0.43	34.09	-	-	-	68.24	3.01
2	0	0.67	0.54	30.25	-	-	-	66.74	2.78
3	0	0.56	0.49	33.76	0.85	0.23	-	74.14	2.83
4	1.32	2.48	2.61	23.46	35.78	0.06	19.43	9.24	-
5	0.17	0.30	0.61	41.09	39.01	0.25	20.0	8.65	-
6	0	0.33	0.42	37 31	39.49	0.25	19.49	8.79	-
7	1.35	0.02	0	0.05	61.09	0.85	28.0	10.89	-

Figure No. 33.   Electron Microprobe Analysis of Specimen No. 326.
Coating Condition - As-Deposited
Nominal Modifier Layer Thickness - 2 Mils
Suspension Ti+V Content - 30 w/o
Sintering Temperature - 2940°F

Spot No.	Distance from Edge (Mils)
1	0.7
2	1.3
3	2.1
4	3.4
5	4 2
6&7	4.8
8	5.8
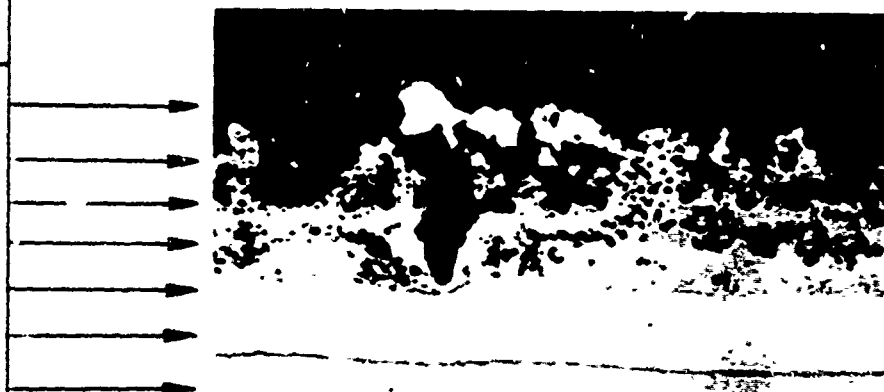
Etch – 15 v/o Lactic Acid + 5 v/o HCl + 5 v/o HNO_3 + 75 v/o H_2O

Magnification – 400X

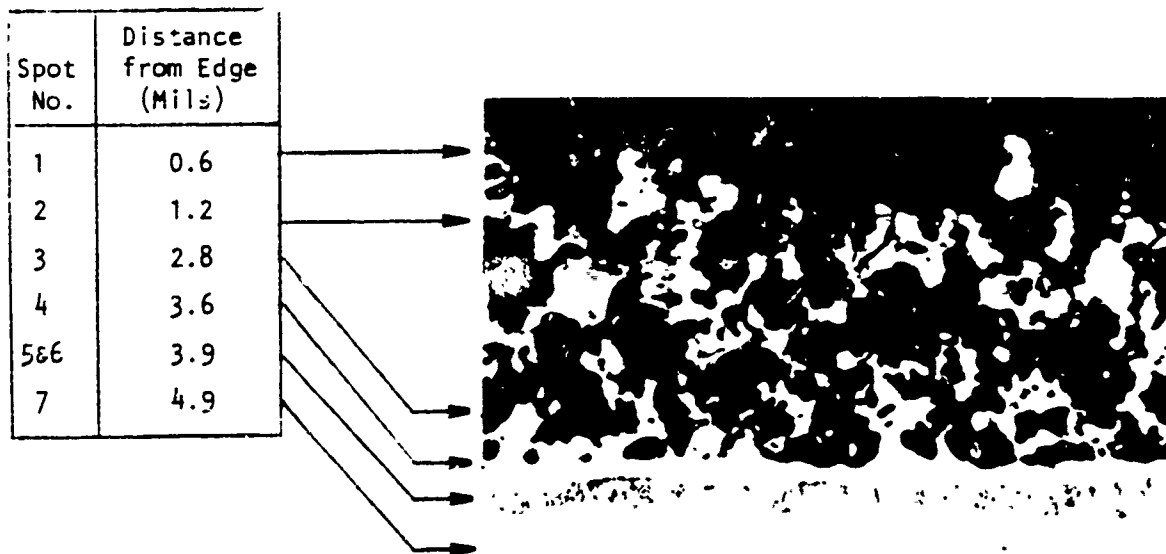| Spot No.	Composition (wt %)								Silicon to Modifier At. Ratio
	Mo	V	Ti	Si	Nb	Zr	Ta	W	
1	6.54	0.14	1.37	45.75	-	-	-	61.57	3.75
2	12.71	0.10	0.42	45.96	-	-	-	58.61	3.54
3	31.48	0.90	0.31	43.87	26.72	-	-	6.88	4.01
4	4.45	2.09	3.72	23.11	46.00	0.17	19.66	12.95	3.49
5	3.06	1.43	1.58	26.87	48.57	0.82	21.51	12.15	-
6	0.32	0.34	0.18	22.55	62.79	0	27.14	9.71	-
7	0.35	0.37	0.18	22.11	61.90	0	26.65	9.48	-
8	0.29	0	0.04	0	61.63	0.70	27.83	10.71	-

Figure No. 34.   Electron Microprobe Analysis of Specimen No. 324.
        Coating Condition – Oxidation Exposed, 20 Hrs at 2500°F
        Nominal Modifier Layer Thickness – 2 Mil
        Suspension Ti+V Content – 30 w/o
        Sintering Temperature – 2940°F

diffusion zone had the highest Ti and V levels with readings ranging from 0.30 to 2.61 w/o and the majority of the readings greater than 1.0 w/o. In most instances, small amounts of Ti and V were found in the inner portions of the diffusion zone and in the substrate adjacent to the diffusion zone. The Mo level in the outer coating was erratic between specimens. Mo levels in the outer coatings of Specimen No. 45 (Figure 31) and No. 326 (Figure 33) ranged from 0 to 6.73 w/o with the majority of the readings being 0 or less than 1.32 w/o. Mo levels in the outer diffusion zone ranged from 1.32 to 3.56 w/o. Higher Mo in the outer diffusion zone was associated with higher Mo contents in the outer coating. Small amounts of Mo were found in the inner diffusion zone and in the substrate adjacent to the diffusion zone.

W content in the outer coating varied on individual specimens but was generally high with the majority of readings above 50 w/o. W levels in the diffusion zone were not too different from the nominal 10.5 w/o of the substrate. Si levels in the outer coating varied on individual specimens and between specimens but were in the range of about 30 to 40 w/o. Si levels in the diffusion zone varied from 22.11 w/o to 41.09 w/o. In most instances, traces of Si were found in the substrate adjacent to the diffusion zone. Silicon-to-modifier atomic ratios calculated from the microprobe analyses were higher than the same ratios calculated from modifier layer and silicon weight gains. For example, the average silicon-to-modifier atomic ratio of the outer coating on specimen No. 45 was 3.54 when calculated from microprobe data, but only 2.33 when calculated from weight gain data (see Table VIII). This difference is due to the assumption that the Ti and V contents of the suspension and modifier layer would be the same and that these elements would not be depleted during the sintering cycle.

The results of microprobe analyses performed on the edges of specimen No. 326 are presented in Figure 35. Comparison of these data with the data obtained from the sides of the specimen (see Figure 33) does not indicate any compositional differences that would result in oxidation failure initiating at the edge. Ti and V in the outer coating was lower at the corners (0.04 to 0.21 w/o compared to 0.43 to 0.50 w/o); however, Ti and V levels in the diffusion zone are comparable at the sides and corners. Mo levels in the outer coating at the corners was erratic but substantially higher than at the sides of the
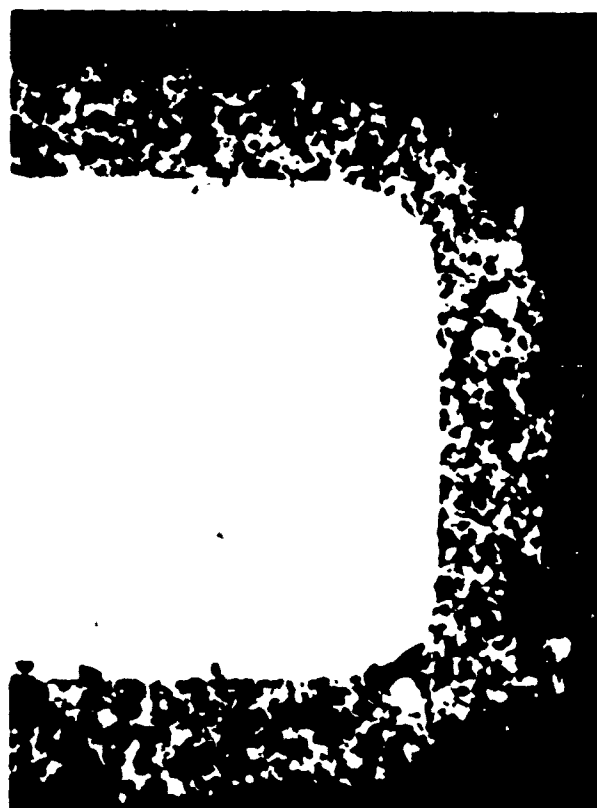
Corner A	
Spot No.	Location
1	Coating
2	"
3	"
4	"
5	Diffusion Zone
6	" "
7	Substrate

Corner B	
Spot No.	Location
1	Coating
2	"
3	"
4	"
5	Diffusion Zone
6	" "
7	Substrate

Magnification - 120X
Etchant - 15 v/o Lactic Acid + 5 v/o
         HCl + 5 v/o HNO_3 + 75 v/o H_2O

Figure 35.   Locations of Electron Microprobe Analyses
                  on Specimen No. 326.
                          Coating Condition - As-Deposited
                          Nominal Modifier Layer Thickness - 2 mils
                          Suspension Ti+V Content - 30 w/o
                          Sintering Temperature - 2940°F

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Corner A									
Spot No.	Composition (wt %)								Silicon to Modifier At. Ratio
	Mo	V	Ti	Si	Nb	Zr	Ta	W	
1	0.06	0.09	0.05	26.27	-	-	-	65.01	2.62
2	44.63	0.04	0.06	37.43	-	-	-	3.54	2.85
3	7.21	0.09	0.05	28.98	0.07	0.04	0.06	54.87	2.74
4	39.84	0.02	0.06	35.93	0.05	0.03	0.07	8.10	2.78
5	2.53	1.15	2.15	25.06	29.95	0.03	7.41	6.41	-
6	0.05	0.09	0.05	35.37	33.66	0.03	15.97	5.28	-
7	0.04	0.02	0.05	0.01	59.83	0.03	26.17	11.27	-

Corner B									
Spot No.	Composition (wt %)								Silicon to Modifier At. Ratio
	Mo	V	Ti	Si	Nb	Zr	Ta	W	
1	0.07	0.21	0.06	28.61	-	-	-	60.21	3.06
2	15.56	0.04	0.06	31.63	-	-	-	41.32	2.90
3	50.85	0.04	0.06	39.07	-	-	-	0.05	2.61
4	1.24	0.04	0.06	24.31	0.07	0.04	0.06	56.82	2.67
5	2.87	2.49	1.97	29.44	28.00	0.03	11.25	5.88	-
6	0.05	0.02	0.06	34.76	33.79	0.03	14.11	5.78	-
7	0.04	0.04	0.05	0.02	54.68	0.14	23.92	10.84	-

Figure 35   (continued)

specimen (0.06 to 50.85 w/o compared to 0 to 1.11 w/o). W levels, although erratic, had comparable maximum values in the corners and at the side of the specimen. Silicon levels and the atomic ratios of Si-to-modifier elements at the corners were similar. Average silicon-to-modifier atomic ratios of the outer coating were 2.74 and 2.81 at the corners compared to 2.87 at the side of the specimens.

Table X compares the results of an electron microprobe analysis on a typical program coating (Specimen No. 45 in Figure 31) with a similar analysis reported for the NS-4 coating[2] deposited by manual dipping in a slurry, sintering and then siliciding by pack cementation. In both instances, the modifier layer was sintered at 2760°F and the coating was in the as-deposited condition. In general, the program coating contained more W but less Ti, V, Mo and Si than the coating deposited by conventional processing.

The average Ti and V levels in the outer coating were 0.86 w/o and 0.73 w/o in the program coating compared to 4 7 w/o and 3.7 w/o in the conventional coating. The inner diffusion zone for the program coating also had lower Ti and V levels than the conventional coating. The outer diffusion zone of the program coating, however, had higher Ti and V levels than the conventional coating (3.59 w/o and 1.93 w/o compared to 2.3 w/o and 1 1 w/o) This higher Ti and V content in the inner diffusion zone is some indication that, while Ti and V levels of the electrophoretic bisques may have been high, these elements were depleted during sintering or during siliciding by the pulsed pressure chemical vapor deposition process. In previous work[2] vanadium was observed to be essential in the coating to prevent pest-type, low temperature (1600°F) oxidation failure. Titanium was reported to contribute to short-term oxidation resistance and activation of the modifier layer for siliciding (increased titanium content increased siliciding rate). The overall low titanium content may have contributed to early oxidation failure of the program coatings through a decrease in short-term oxidation resistance as well as decreasing si' cor weight gain in the outer coating.

The average silicon level in the uter coating was 40 79 w/o compared to 51.1 w/o in the conventional NS-4 coat . though silicon levels in the outer diffusion zone were higher in the program coating and si con levels in the inner diffusion zones were mparable in the two coatings, primary oxidation protection

TABLE X

COMPARISON OF THE CHEMICAL COMPOSITION OF THE NS-4 COATING ON FS-85 DEPOSITED BY TWO DIFFERENT PROCESSING TECHNIQUES

Area	Coating(a)	Element(b) (w/o)										Average Atomic Ratio Si/Mod
		Ti		V		Mo		W		Si		
		Range	Avg	Range	Avg	Range	Avg	Range	Avg	Range	Avg	
Outer Coating	Electrophoretic + CVD	0.22/1.93	0.86	0.67/0.73	0.70	0-6.73	6.09	61.03/65.89	63.97	35.57/43.76	40.79	3.54
	Dip + Pack	0.30/6.7	4.7	1.5/4.0	3.1	0-36.3	21.8	0/65.2	53.8	34.2/68.2	51.1	3.9
Outer Diffusion Zone	Electrophoretic + Dip + Pack	-	3.59	-	1.93	-	1.60	-	8.97	-	24.60	
	Dip + Pack	-	2.3	-	1.1	-	-	-	6.2	-	40.3	
Inner Diffusion Zone	Electrophoretic + CVD	-	0.06	-	0.02	-	0.05	-	6.15	-	37.74	
	Dip + Pack	-	2.3	-	0.07	-	-	-	3.6	-	38.8	

NOTES

(a) Electrophoretic + CVD - Specimen No 45 (Figure 79), Sintering Temperature = 2760°F.

Dip + Pack - From Reference (2), Sintering Temperature 2760°F.

(b) Averages for outer coating only; others are the result of one reading.

Spots with 0 w/o were not included in the averages for the outer coating.

is provided by silicon in the outer coating. The poor oxidation life of the program coatings is attributed to this low silicon content in the outer coating.

The program coating contained less Mo (6.09 w/o compared to 21.8 w/o) but more W (63.97 w/o compared to 53.8 w/o) in the outer coating. In the previous work[2] it was observed that the W/Mo ratio could be varied over wide limits without affecting oxidation resistance. It is reasonable to assume that these differences in Mo and W content did not contribute to the poor oxidation resistance of the program coatings.

As discussed above, poor oxidation resistance of the program coatings was attributed to insufficient silicon. In addition to the chemical vapor deposition equipment limitations as described in Section 3.3.2, it appears that the Ti and V contents of the program coatings would have to be increased to improve high temperature (2500°F) oxidation resistance, low temperature (1600°F) pest-type oxidation resistance and silicon deposition rate. In addition to loss of these elements during vacuum sintering of the modifier layer, some portion of these elements was probably lost through cyclic evacuation during chemical vapor deposition of silicon. In order to increase the levels of Ti and V in the coating, the levels of these elements would have to be increased in the as-deposited modifier layer to compensate for these losses. This could be accomplished by increasing the Ti and V contents of the electrophoretic suspension.

4.0   SUMMARY OF RESULTS

The following summation can be made from the experimental work performed
on this program.

1. The modifier layer (W+Mo+Ti+V) could not be deposited by electro-
   phoresis from waterbase suspensions. Gases resulting from electrol-
   ysis of the water produced defects in deposits made from these
   suspensions.

2. The modifier layer could be satisfactorily deposited by electro-
   phoresis from isoproponol-nitromethane suspensions.

3. Increasing the sintering temperature from 2760 to 2940°F resulted
   in ro detectable difference in modifier layer thickness through
   vaporization losses or more complete sintering. The higher sintering
   temperature did result in diffusion of Mo into the substrate during
   the sintering cycle. Ti and V diffused into the substrate at both
   sintering temperatures, while W did not diffuse into the substrate
   at either sintering temperature. Both sintering temperatures provided
   some homogenization of the modifier layer elements.

4. The silicon to modifier atomic ratio obtained from chemical vapor
   deposition of silicon was a function of modifier layer variations,
   $H_2/SiCl_4$ ratio, reaction chamber pressure and deposition time.
   Decreases in modifier layer thickness and Ti+V content and the
   $H_2/SiCl_4$ ratio increased the silicon to modifier atomic ratio.
   Increases in reaction chamber pressure up to 0.400 atm increased
   the silicon to modifier atomic ratio. The effect of deposition time
   was dependent on reaction chamber pressure. At a reaction chamber
   pressure of 0.167 atm, increasing the depositon time increased the
   silicon to modifier atomic ratio to a limiting value, but at 0.400
   atm increasing the deposition time increased the silicon to modifier
   ratio for all deposition times investigated.

5. Using a $H_2/SiCl_4$ ratio of 21, a reaction chamber pressure of 0.400
   atm and a deposition temperature of 2300°F, deposition times of up

to 10 hours were required to produce silicon to modifier atomic
ratios as high as 3.0 for 2 mil thick modifier layers deposited
from suspensions containing a Ti+V content of 10 w/o. Using the
same deposition parameters, a silicon to modifier layer atomic
ratio of 2.5 could be obtained in 2.0 mil thick modifier layers
deposited from suspensions containing a Ti+V content of 20 w/o.
Using the same deposition time of 7.5 hours, a silicor to modifier
layer atomic ratio of >2.1 could be obtained in a 2.0 mil thick
modifier layer deposited from a suspension containing a Ti+V
content of 30 w/o. Projected deposition times of 15-20 hours
would be required to obtain these silicon to modifier atomic
ratios in heavier modifier layers.

6. Coated coupons exposed at $2500^{\circ}F$ in a static air atmosphere failed
within 20 hours of exposure. Premature failure was attributed to
the low silicon content of the coatings.

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5.0   CONCLUSIONS AND RECOMMENDATIONS

The major obstacle to accomplishing the program objectives was the inability to deposit sufficient silicon on the modifier layer using the present chemical vapor deposition equipment. The equipment would have to be modified to better withstand the severe service environment resulting from the high temperature and extended deposition times necessary to obtain higher silicon contents in the modifier layers. Based on previous work with the NS-4 coating deposited by conventional processing techniques and electron microprobe analyses performed on the program coatings, there is some indication that increasing the Ti level in the modifier layer could increase the rate of silicon weight gain. Nevertheless, equipment modification would probably still be necessary.

Electrophoretic deposition from isopruponol-nitromethane suspensions produced satisfactory modifier layer deposits in respect to thickness. However, the green strength (before sintering) could be improved by adding a resin binder to the suspension. This would increase the handling losses prior to sinter'ng and result in a more uniform modifier layer thickness. Addition of a resin to the suspensions would require modification of the deposition parameters. In addition to raising the Ti level in the coating, additional testing at low temperatures (1600°F) for pest-type oxidation resistance may indicate a need to increase the vanadium content in the coating. This could be accomplished by increasing the Ti and V content of the electrophoretic suspension.

This program has demonstrated that the modifier layer of the NS-4 coating can be deposited by electrophoretic deposition. In addition to cost savings through the use of less labor and better materials utilization, this process has the potential to deposit uniform coatings on internal surfaces. In lieu of modifying the chemical vapor deposition equipment, the electrophoretic process could be used in combination with pack siliciding to deposit the NS-4 coating. By using pack siliciding, there may not be any need to increase the Ti and V contents of the electrophoretic suspensions, since it is probable that some of the Ti and V .n the modifier layer was lost during chemical vapor deposition of silicon.

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